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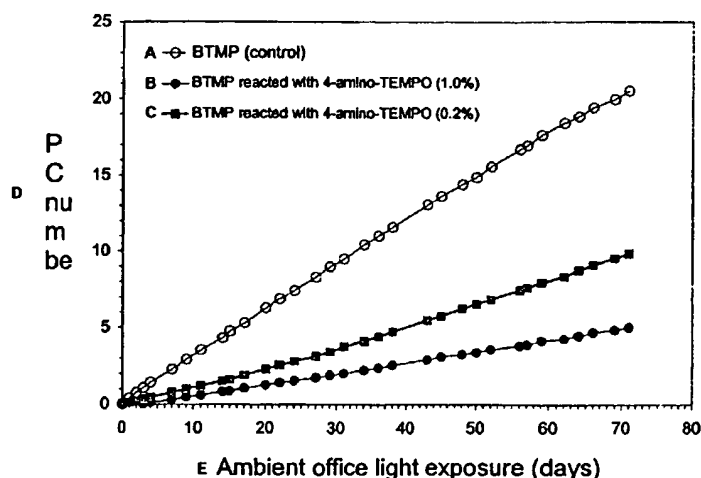
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(54) Title: LIGHT-STABLE LIGNOCELLULOSIC MATERIALS AND THEIR PRODUCTION



(57) Abstract: A novel method for the production of light-stable lignocellulosic materials, in particular, the production of mechanical wood pulps with much improved light stability is described, as well as the resulting pulps of improved light stability and papers containing such pulps. The novel method involves the reaction of lignocellulosic materials such as bleached thermomechanical pulp (BTMP) with a water-soluble, fibre-reactive yellowing inhibitor possessing a primary or secondary amino ($-NH_2$ or $-NHR$) functional group in an aqueous medium, or with a water-soluble, fibre-reactive hindered amine light stabilizer possessing a primary or secondary amino ($-NH_2$ or $-NHR$) functional group in an alkaline peroxide bleaching medium or in an aqueous medium with a subsequent bleaching of the materials in an alkaline peroxide bleaching medium. Examples of such water-soluble, fibre-reactive yellowing inhibitors and hindered amine light stabilizers are the commercially available 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl (4-amino-TEMPO) and 4-amino-2,2,6,6-tetramethylpiperidine, respectively.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

LIGHT-STABLE LIGNOCELLULOSIC MATERIALS AND THEIR PRODUCTION

BACKGROUND OF THE INVENTION

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TECHNICAL FIELD

The current invention relates to the field of wood, pulp and paper production. More specifically, it relates to the production of light-stable lignocellulosic materials, in particular, the production of mechanical wood
10 pulps and papers with much improved light stability, as well as to the resulting pulps and papers having improved light stability.

BACKGROUND ART

The primary components of wood are the fibrous, hydrophilic
15 carbohydrates (cellulose and hemicelluloses) and the three-dimensional, hydrophobic lignin. For the purpose of making papers, wood, either in the form of whole logs, wood chips or sawmill residues, must first be reduced to pulps (discrete fibres) by a chemical or mechanical pulping process. In chemical pulping of wood, pulps are produced in a yield of 45-55% through
20 the dissolution of lignin by the pulping chemicals. One example of chemical pulps is the so-called kraft pulp produced from the kraft pulping process where sodium hydroxide and sodium sulfide are used as the pulping chemicals. In mechanical pulping of wood, pulps are formed in a yield of 90-98% through the action of mechanical forces that separate the fibres but
25 retain lignin. Examples of mechanical wood pulps are the thermomechanical pulp (TMP) produced from the thermomechanical pulping process and the chemithermomechanical pulp (CTMP) produced from the chemithermomechanical pulping process. Depending on their end uses, papers are produced from chemical wood pulps or mechanical wood

pulps, or a combination of both, together with various papermaking additives.

High-yield, lignin-containing mechanical wood pulps have a light, yellow-brown colour. Bleaching of these pulps to a whiter colour is necessary if they are to be used alone or in combination with bleached chemical pulps to make high-quality papers. The whiteness of pulps and papers is commonly estimated by ISO brightness determination which measures the directional reflectance of light at 457 nm of the papers [TAPPI Test Methods, T452 om-92, Tappi Press: Atlanta, 1996]. Unbleached, lignin-containing mechanical wood pulps have ISO brightness values between 45-65%, depending on the wood species and the pulping conditions.

The current industrial processes for the bleaching of mechanical wood pulps are the alkaline hydrogen peroxide process and the sodium hydrosulfite process with the former being the superior one in terms of brightness gain [Presley and Hill in: *Pulp Bleaching – Principle and Practice*, ed. Dence and Reeve, p. 459, Tappi Press: Atlanta, 1996]. Alkaline hydrogen peroxide, in the presence of peroxide stabilizers such as sodium silicate and magnesium sulfate, is capable of bleaching mechanical wood pulps such as spruce TMP from an initial brightness of 55-60% to 70-80%. Alkaline hydrogen peroxide bleaching of mechanical wood pulps can be carried out in a single-stage or multistage in one or more than one refiner, bleach tower, storage vessel, dryer or mixer. Alternatively, the bleaching chemicals can also be impregnated into the wood chips in one or more than one impregnator and the bleaching achieved during impregnation before refining [Bohn, CPPA 1990 Annual Meeting Preprints, B109 – B114, Montreal, Quebec, 1990].

High-yield, lignin-containing mechanical wood pulps, unbleached or bleached, have properties such as high opacity (low show-through) that are

desirable for the production of printing and writing papers. However, papers produced from mechanical pulps yellow (lose their brightness) rapidly when exposed to light. Such a light-induced yellowing has limited the wider use of mechanical wood pulps in high-quality papers such as printing and writing papers.

The light-induced yellowing (brightness reversion) of lignin-containing mechanical wood pulps is known to be due to the oxidation of lignin. Over the past fifty years or so, many methods have been reported for the improvement of the light/brightness stability of mechanical wood pulps or papers. These methods involve either a chemical treatment on pulps aimed at the modification of the yellowing-causing lignin functional groups or a surface treatment on papers made from mechanical pulps with yellowing inhibitors such as an UV absorber [Heitner, in: *Photochemistry of Lignocellulosic Materials*, ed. Heitner and Scaiano, p.192 - 204, ACS Symposium Series 531, ACS 1993].

European patent, No. 0,280,332, published on August 31, 1988 describes a pulp chemical treatment method that improves the light/brightness stability of peroxide-bleached mechanical wood pulps. This pulp treatment method involves the reduction of lignin α -carbonyl and (-carbonyl groups with sodium borohydride, the blocking of the phenolic hydroxyl groups with gaseous ethylene or propylene oxide and, in some cases, the application of a fluorescent chemical. The treatment is rather complicated with washing, dewatering and temperature adjustment between the borohydride and the gaseous ethylene or propylene oxide treatment.

Several paper surface treatment methods that improve the light/brightness stability of papers made from mechanical pulps have been described. One example of these methods can be found in United States patent, No. 5,080,754, issued on January 14, 1992. The method comprises

the steps of forming mechanical pulps into a paper sheet and treating the paper sheet with a formyl compound yellowing inhibitor by spraying the inhibitor in a solution or solid form onto the paper sheet. Although this method and many other surface treatment methods reported elsewhere are effective in improving the brightness stability of the papers, the methods can not be applied to pulps and thus are of no use to pulp mills that only produce mechanical pulps. In addition, because high-quality papers need to contain some chemical wood pulps to give other desired properties such as sheet smoothness and strength, application of yellowing inhibitors to such papers is deemed less efficient as some of the inhibitors will be wasted to cover the surface occupied by the light-stable chemical wood pulps.

PCT, WO 99/05108, of Ciba Specialty Chemicals and published Feb. 4, 1999 and US Patent, No. 6,254,724B1 issued to Ciba Specialty Chemicals on July 3, 2001 describe the use of hindered nitroxide radicals, particularly derivatives of 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (4-hydroxy-TEMPO) as effective yellowing inhibitors alone or when combined with an UV absorber and other coadditives. All the examples provided in these publications involve syringe-injecting/spraying of an inhibitor solution to already-formed paper sheets, similar to other paper surface treatment methods reported elsewhere in the prior art. Although the descriptions are broad, indicating that the extremely broad class of inhibitors can be added to pulps, pulp slurries and papers, at all possible manufacturing stages, there is no teaching of how the inhibitors might be successfully applied to pulp slurries and retained by the pulps. From these publications, it is not evident at all how the inhibitors, particularly those water-soluble ones, can be retained by pulp fibres on pulp slurries in aqueous media. The actual teachings are of coating the paper sheets with the inhibitors. It has recently been concluded that the inhibitor system based on hindered nitroxide radicals has no affinity for pulp fibres and thus

must be applied to the surface of already-formed papers, in the press or dryer section of the paper machine, or on an off-line coater [Yuan *et al.*, *Proceedings to 87th PAPTAC Annual Meeting*, Montreal, Quebec, C43-C52, 2001].

5 Hindered nitroxide radicals have deep orange colors and are known to be much less desirable yellowing inhibitors than their more expensive, colorless hydroxyamine derivatives. Surface coating of 1.0%, by wt. (based on pulp) of 4-hydroxy-TEMPO to paper sheets has been shown to cause the brightness of the sheets to drop by about 7 ISO points [Cunkle, *et al.*,
10 *Proceedings to 10th International Symposium on Wood and Pulping Chemistry, Vol. 1*, 718-721, 1999]. Colorless hydroxyamine derivatives of nitroxide radicals are prepared by treatment of the radicals with a reducing agent such as a metal hydride [Rozantsev, in: *Free Nitroxyl Radicals*, p. 94, ed. Ulrich, Plenum Press, New York, 1970].

15 Hindered amine light stabilizers (HALS) have been widely used for the light stabilization of synthetic polymers such as polyolefins [Minagawa, *Polymer Degradation and Stability* 25: 121-141, 1989]. Application of hindered amine light stabilizers to papers made from lignin-containing mechanical wood pulps, however, was found to have no or even a
20 detrimental effect on the brightness stability of the papers [Fornier De Violet, *et al.*, *Cellulose Chem. Technol.* 24: 225-235, 1990].

 The light-induced yellowing (brightness reversion) of mechanical wood pulps is known to be due to the oxidation of lignin phenoxy radicals generated from lignin phenols and \forall -carbonyl or \forall -hydroxyl- \exists -O-4 ethers
25 to the yellow *o*-quinones [Leary, *J. Pulp Paper Sci.* 20(6): J154-160, 1994]. Chemical modifications of the yellowing-causing lignin functional groups such as the reduction of lignin \forall -carbonyl groups by borohydride and the blocking of the lignin phenolic hydroxyl groups by gaseous ethylene oxide

can be performed on pulps to give mechanical pulps with improved brightness stability. However, the modifications of lignin functional groups require the use of a large amount of chemical reagents and a rather complicated treatment procedure. The use of yellowing inhibitors such as
5 UV absorbers and/or radical scavengers to prevent the formation and/or the oxidation of the phenoxy radicals is an alternative method for yellowing inhibition. However, one drawback of such a method is that it is only applicable to already-formed papers.

UV absorbers possessing an epoxide or isocyanate functional group
10 have been grafted to the surface of wood in organic media to improve the light stability of the wood [Williams, *J. Appl. Polym. Sci.* 28: 2093-2103, 1983; Grelier, *et al.*, *Holzforschung* 51: 511-518, 1997].

PCT, WO 00/40618, issued July 13, 2000 reports the introduction of a primary amino group (NH_2) into mechanical wood pulps via the reactions
15 of the pulps sequentially with epichlorohydrin and ammonium hydroxide. The chemically modified pulps, which are insoluble in aqueous media, could be blended with the unmodified mechanical wood pulps to provide pulps with improved strength properties. The improved strength properties were speculated to be due to the cross-linking (formation of imino $\text{C}=\text{N}$
20 bonds) between the amino groups in the modified pulps with the carbonyl groups in the unmodified pulps. The reaction of a carbonyl ($\text{C}=\text{O}$) group and a primary amino (NH_2) group to give an imine (imino bond) ($\text{C}=\text{N}$) and water (H_2O) is known to be a reversible (equilibrium) reaction [Kemp and Vellaccio, *in Organic Chemistry*, p. 289, Worth Publishers Inc., New York,
25 1980]. As such, the formation of imine is highly unfavorable in the presence of additional water.

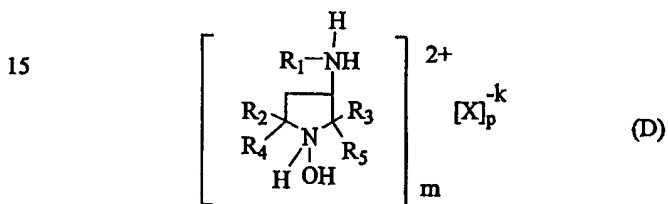
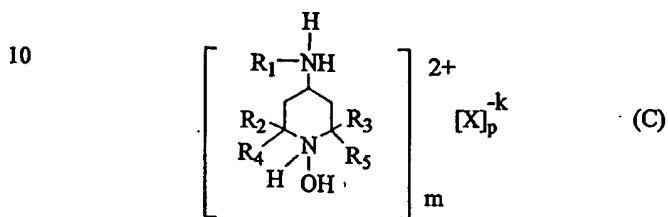
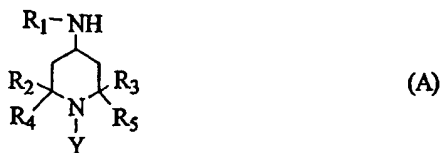
DISCLOSURE OF THE INVENTION

This invention seeks to provide a method for the production of a light-stable lignocellulosic material.

The invention also seeks to provide novel lignocellulosic material
5 obtainable by the method of the invention.

The invention further seeks to provide a paper containing the novel lignocellulosic material of the invention.

In accordance with one aspect of the invention, there is provided a method for the production of light-stable, lignocellulosic materials such as
10 mechanical wood pulps comprising reacting the materials with a water-soluble, yellowing inhibitor possessing a primary or secondary amino group of the formula A, B, C or D wherein Y is oxyl (O[•]) or hydroxyl (OH) in an aqueous medium, or with a water-soluble hindered amine light stabilizer of the formula A or B wherein Y is hydrogen (H) in an alkaline peroxide
15 bleaching medium or in an aqueous medium with a subsequent bleaching of the materials in an alkaline peroxide bleaching medium:



25

wherein R_1 is hydrogen or an alkyl group $(CH_2)_nH$ that is unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber, R_2 , R_3 , R_4 and R_5 are independently alkyl group $(CH_2)_nH$ that are unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, amino, ester, amide, carboxyl and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber; X is an inorganic or organic anion, n is 1 to 14, preferably 1 to 6, and more

preferably 1 to 4, k is 1 to 3, p is 1 or 2, M is an ammonium or metal ion, and r is 1, 2 or 3, and the total charge of $2m$ is equal to kp .

In another aspect of the invention, there is provided a novel lignocellulosic material, for example, a pulp obtained by the method of the
5 invention.

In still another aspect of the invention, there is provided a paper containing the novel lignocellulosic material.

DESCRIPTION OF BEST MODES

10 In one embodiment, the present invention produces light-stable lignocellulosic materials such as various wood products and mechanical wood pulps by developing water-soluble, fibre-reactive yellowing inhibitors and attaching them to the lignocellulosic materials, for example wood pulps, in aqueous media. The resulting light-stable mechanical wood pulps
15 can then be used to make papers composed mainly of mechanical wood pulps, including high quality printing and writing papers as well as newsprint and telephone directory, with improved brightness stability. These pulps can also be used to replace a part of the chemical wood pulps in high-quality papers such as printing and writing papers.

20 It has now been discovered that lignocellulosic materials such as mechanical wood pulps with much improved light/brightness stability can be produced by reaction of the material with a water-soluble, fibre-reactive yellowing inhibitor possessing a primary or secondary amino ($-NH_2$ or $-NHR$) functional group in an aqueous medium, or with a water-soluble,
25 hindered amine light stabilizer (HALS) possessing a primary or secondary amino ($-NH_2$ or $-NHR$) functional group in an alkaline peroxide bleaching medium, or in an aqueous medium with a subsequent bleaching of the material in an alkaline peroxide bleaching medium.

Alkaline peroxide bleaching medium in the present specification contemplates the medium used for a single-stage or multi-stage alkaline hydrogen peroxide bleaching of wood pulps in one or more than one refiner, bleach tower, pulp mixer, and/or any other vessel or the medium
5 used for a single-stage or multi-stage alkaline hydrogen peroxide impregnation of wood chips in one or more than one impregnator. An aqueous medium in the present specification includes the said alkaline peroxide bleaching medium.

Thus in one aspect of the invention there is provided a method for
10 the production of a light-stable lignocellulosic material such as mechanical wood pulp comprising reacting the material with a water-soluble yellowing inhibitor possessing a primary or secondary amino group in an aqueous medium, or with a water-soluble hindered amine light stabilizer possessing a primary or secondary amino group in an alkaline peroxide bleaching
15 medium or in an aqueous medium with a subsequent bleaching of the material in an alkaline peroxide bleaching medium.

In another aspect of the invention there is provided a light-stable, lignin-containing mechanical wood pulp comprising a lignin-containing mechanical wood pulp having a water-soluble yellowing inhibitor
20 possessing a primary or secondary amino group, said inhibitor being linked to said pulp via said amino group.

In other aspects of the invention there is provided a paper sheet in which the pulp component comprises a pulp of the invention, as described hereinbefore, as the sole pulp component or in conjunction with chemical
25 wood pulp.

Paper sheet in the present specification contemplates paper or paperboard.

Thus, in accordance with the present invention, water-soluble, fibre-reactive yellowing inhibitors and hindered amine light stabilizers are

provided that are capable of forming covalent bonds to and thus being retained by lignocellulosic materials such as mechanical wood pulp fibres in aqueous media. Prior to the present invention, no yellowing inhibitors possessing an epoxide, isocyanate, or any other functional groups have been attached to wood pulp fibres, either in organic or in aqueous media. Also prior to the present invention, hindered amine light stabilizer has been found to be detrimental to the brightness stability of papers made from mechanical pulps. No hindered amine light stabilizer has previously been used in any pulping or bleaching process to make pulps or papers.

Unexpectedly and surprisingly, it has been found, during attempts to attach 4-amino-TEMPO to mechanical wood pulps via sequential reactions of the pulps with the sodium salt of 4-[2'-(4',6'-dichloro-s-triaznyl)]amino-benzene sulfonic acid and 4-amino-TEMPO, that brightness stability improvement is achieved by the reaction between the pulp fibres and the water-soluble 4-amino-TEMPO. It has also been discovered that water-soluble yellowing inhibitors possessing a primary or a secondary amino ($-NH_2$ or $-NHR$) group are extremely reactive towards lignocellulosic materials and they can be chemically attached to the materials with great ease in an aqueous medium. Furthermore, it has been discovered that lignocellulosic materials with improved light/brightness stability can be produced by reacting the materials with a hindered amine light stabilizer possessing a primary or secondary amino ($-NH_2$ or $-NHR$) group in an alkaline peroxide bleaching medium, or in an aqueous medium with a subsequent bleaching of the materials in an alkaline peroxide bleaching medium.

The present invention is based on such surprising discoveries.

The importance of the amino group in providing the fibre-reactivity to the yellowing inhibitors is explicitly demonstrated in examples 1 and 2 of the present invention where 4-amino-TEMPO but not 4-hydroxy-TEMPO is

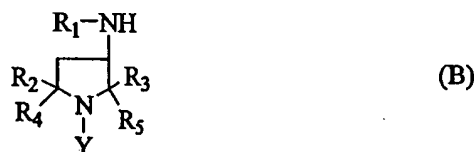
shown to be reactive towards mechanical wood pulp fibres. Pulps reacted with 4-amino-TEMPO in aqueous media and then washed repeatedly with water retain a significant amount of the radical scavenger (as indicated by the increased nitrogen content of the pulps) and show much higher
5 brightness stability than the control samples. Under identical conditions, pulps treated with 4-hydroxy-TEMPO do not retain any of the reagent and do not show any improved brightness stability. The importance of the amino group in providing the fibre-reactivity to hindered amine light stabilizers is also explicitly demonstrated in example 25 of the present
10 invention where addition of 4-amino-2,2,6,6-tetramethylpiperidine, but not 4-oxo-2,2,6,6-tetramethylpiperidine, to an alkaline peroxide bleaching of the pulp is shown to provide the pulp with improved brightness stability.

The unexpected facile reaction between the water-soluble, yellowing inhibitors or hindered amine light stabilizers (HALS) possessing a primary
15 or secondary amino ($-NH_2$ and $-NHR$) group and lignocellulosic materials such as mechanical wood pulps in aqueous media as discovered in the present invention, appears to be due to a type of reaction that is unaffected or accelerated by the presence of water.

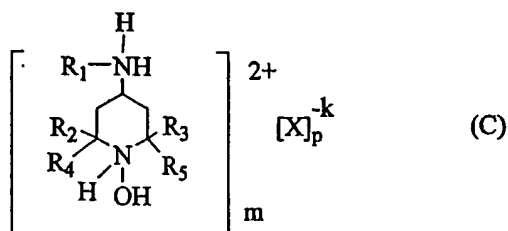
In particular embodiments of the present invention, lignocellulosic
20 materials such as mechanical wood pulps with much improved light/brightness stability can be produced by reaction with a water-soluble, yellowing inhibitor possessing a primary or secondary amino ($-NH_2$ or $-NHR$) functional group of the formula A, B, C or D wherein Y is oxyl (O^\cdot) or hydroxyl (OH) in an aqueous medium, or with a water-soluble hindered
25 amine light stabilizer (HALS) of formula A or B wherein Y is hydrogen (H) in an alkaline peroxide bleaching medium or in an aqueous medium with a subsequent bleaching of the materials in an alkaline peroxide bleaching medium:



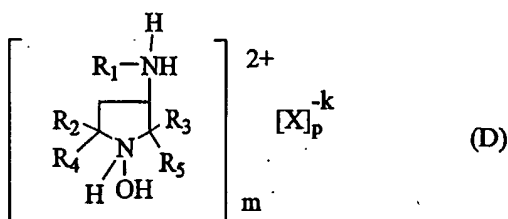
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wherein R_1 is hydrogen or an alkyl group $(\text{CH}_2)_n\text{H}$ that is unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl and/or carboxylate $[(\text{COO})_r\text{M}^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber such as 2,4-dihydroxybenzophenone; R_2 , R_3 , R_4 and R_5 are independently alkyl groups $(\text{CH}_2)_n\text{H}$ unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl and/or carboxylate $[(\text{COO})_r\text{M}^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber, such as 2,4-dihydroxybenzophenone; X is an inorganic

or organic anion, such as carbonate, bicarbonate, chloride, bisulfate, sulfate, formate, acetate, citrate, phosphate, oxalate, ascorbate, n is 1 to 14, preferably 1 to 6, and more preferably 1 to 4, k is 1 to 3, p is 1 or 2, M is an ammonium or metal ion, especially an alkali metal or alkaline earth metal ion, r is 1, 2 or 3, and the total charge of $2m$ is equal to the total charge of kp .

In this specification, a "radical derived from an organic ultraviolet absorber" means a radical of the absorber which has the ultraviolet absorbing characteristic of the absorber and thus introduces such characteristic into the inhibitor or stabilizer of formulae A to D.

One example of the water-soluble, fibre-reactive yellowing inhibitors is the commercially available radical scavenger, 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl (4-amino-TEMPO) (available from Aldrich). The reactions of the inhibitors with the lignocellulosic materials can be suitably carried out at a temperature of 20 - 120 °C and a consistency of 1.5 to 40% in an alkaline peroxide bleaching medium or an aqueous medium in a pH range of 3.5-12.5. The inhibitor charge can suitably range from 0.01 to 2.0% by weight based on oven-dried (OD) lignocellulosic material, e.g. pulp weight, preferably at least 0.05%, more preferably at least 0.1% and most preferably from 0.2 to 1.0%, by weight. The reaction may conveniently be carried out in a time of 5 minutes to several days (e.g. 3 to 5 days). Unexpectedly and surprisingly, mechanical wood pulps reacted with yellowing inhibitors of formula A or B where Y is oxyl such as 4-amino-TEMPO have initial ISO brightness similar to or only slightly lower than the control pulps. Only reactions of the pulps with $\geq 0.5\%$ (OD pulp) of 4-amino-TEMPO and at pH ≥ 6.5 cause a small drop (1.0 - 3.0 ISO brightness points) in the initial brightness. Such an unexpected, much less detrimental effect of 4-amino-TEMPO and other nitroxide radicals of

formula A or B on the initial brightness of the inhibitor-attached pulps is explicitly demonstrated in example 4. A BTMP pulp reacted with 1% (OD pulp) of 4-amino-TEMPO has an ISO brightness only 1.9 points lower than the control pulp compared to a drop of 7.1 ISO brightness points when a sheet is coated with 1% (OD pulp) of 4-amino-TEMPO. The brightness stability of the pulp reacted with 4-amino-TEMPO is similar to that of the sheet coated with 4-amino-TEMPO.

It has also been found that the small drop in initial brightness when pulps are reacted with $\geq 0.5\%$ (OD pulp) of 4-amino-TEMPO or other nitroxide radicals of formula A or B at $\geq \text{pH } 6.5$ can be avoided by carrying out the reaction in the presence of, or followed by a separate treatment using a reducing agent such as ascorbic acid or sodium borohydride. The small drop in initial brightness when pulps are reacted with $\geq 0.5\%$ (OD pulp) of 4-amino-TEMPO can also be avoided by carrying out the reaction at $\text{pH} < 6.5$ by addition to the reaction media of, or by treating the resulting pulps with a small amount of an organic or inorganic acid such as citric acid, hydrochloric acid or sulfurous acid in the form of aqueous sulfur dioxide (SO_2).

The reaction with the inhibitor may be carried out in the presence or absence of air or oxygen.

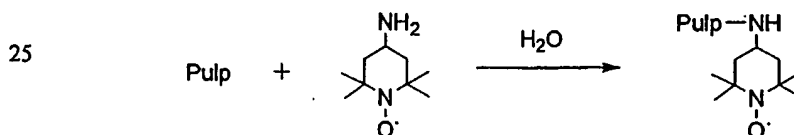
One example of the said water-soluble, fibre-reactive, hindered amine light stabilizers (HALS) (formulas A and B where Y is hydrogen) is 4-amino-2,2,6,6-tetramethylpiperidine (available from Aldrich). The reactions of HALS with lignocellulosic materials can be carried out similarly to the reactions of the yellowing inhibitors. The alkaline peroxide bleaching media used for the reactions of the said fibre-reactive yellowing inhibitors or HALS with and the bleaching of, mechanical wood pulps can be carried out at a temperature of $20 - 120^\circ\text{C}$, a consistency of $1.5 - 50\%$

and a bleaching time of five minutes - several days. The alkaline peroxide impregnation of the wood chips in the presence of the said yellowing inhibitors or hindered amine light stabilizers can be carried out at a temperature of 40 - 90 °C, a solid content of 30 - 60%, by weight, and an
5 impregnation time of five minutes to two hours. The charge of bleaching or impregnation chemicals, hydrogen peroxide, sodium hydroxide (or hydroxide or oxide of other metals), sodium silicate and magnesium sulfate can be varied depending on the target brightness, the economics, the mill configurations and other process conditions. The charge of a fibre-reactive
10 yellowing inhibitor or hindered amine light stabilizer can suitably range from 0.05 to 2.0% by weight based on oven-dried (OD) pulp weight, preferably from 0.1 to 1.0%, by weight.

The reaction with the stabilizer, and the bleaching can be carried out in the presence or absence of air or oxygen.

15 Further according to the present invention, mechanical wood pulps with nearly complete brightness stability can be produced by reaction with the said yellowing inhibitors or HALS, and then by coating of the paper made from the resulting pulps with an organic or inorganic ultraviolet absorber, if R₁, R₂, R₃, R₄ and R₅ in the said yellowing inhibitors or HALS
20 do not contain an organic ultraviolet absorber.

In the particular use of 4-amino-TEMPO the modified pulp may be produced in accordance with Scheme 1 below.



Scheme 1. Attachment of 4-amino-TEMPO to mechanical pulps.

The invention contemplates this method, the modified pulp and paper containing the modified pulp.

The modified pulp of the invention may be the sole pulp component of a paper sheet formed from the pulp, or it may be employed in conjunction with chemical wood pulp. Thus the paper may have a pulp component comprising 1 to 100% by weight of the modified pulp of the invention and 0 to 99%, by weight of a chemical wood pulp, to a total of 100%.

It has also been found advantageous to react *in-situ* or treat the pulp reacted with $\geq 0.5\%$ (OD pulp) of the inhibitors of formulas A and B where Y is oxyl with a reducing agent such as ascorbic acid or sodium borohydride, or an acid such as hydrochloric acid or citric acid.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 shows the post colour (PC) numbers versus ambient office fluorescent light exposure times of a spruce bleached thermomechanical pulp (BTMP) and the BTMP pulps reacted, respectively, with 1.0% and 0.2% (based on pulp) of a water-soluble yellowing inhibitor, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) to produce modified pulps of much improved light/brightness stability in accordance with the invention;

FIG. 2 shows the ISO brightness values versus light exposure times of the same pulps;

FIG. 3 shows the ISO brightness values versus ambient office light exposure times of a spruce BTMP and a spruce BTMP pulp bleached in the

presence of 1.0%, by wt., (based on pulp) of a hindered amine light stabilizer, 4-amino-2,2,6,6-tetramethylpiperidine to produce a bleached pulp of improved brightness/light stability in accordance with the invention; and

5 FIG. 4 shows the PC numbers versus light exposure times of the same pulps.

EXAMPLES

The present invention is illustrated but not limited by the following
10 examples:

General Procedure A Employed in the Examples: Reaction at Low Consistency

Unless otherwise specified, a known amount of a mechanical wood pulp is mixed with deionized water to give a pulp consistency of 1.5%.
15 "Consistency" is the weight percentage of pulp in a pulp and water mixture. The pulp slurry is purged with N₂ and kept at room temperature (~ 20 °C) or heated to a desired temperature. A said water-soluble, yellowing inhibitor or HALS (0.01 - 2.0% on pulp) is added. The pH of the pulp slurry is adjusted to a desired value (3.5 - 12.5) by addition of a small amount of
20 NaOH or 6% SO₂ solution. The pulp slurry is stirred for 3 hours unless otherwise specified. The pH of the pulp slurry is then adjusted to near neutral (pH 6.5 - 7.0) when necessary. The pulp slurry is diluted, unless otherwise specified, with deionized water to 0.5 to 1.0% consistency, filtered and washed with deionized water. Unless otherwise specified, the
25 filtered pulp is diluted with deionized water, stirred and filtered two more times.

General Procedure B Employed in the Examples: Reaction at Medium to High Consistency

A said water-soluble yellowing inhibitor or HALS (0.01 – 2.0% on pulp) is dissolved in a known amount of deionized water that when mixed with a mechanical pulp will give a desired consistency (5.0 to 40% consistency). The pH of the inhibitor solution is adjusted to a desired value and the inhibitor solution is added to the pulp in a polyethylene bag. The bag is sealed and immersed in a hot water bath set at 40 °C for 3 hours, unless otherwise specified, with manual mixing of the pulp every hour. The bag is then removed and cooled in a cold water bath to room temperature (~20 °C). The pH of the pulp slurry is adjusted to near neutral (pH 6.5 – 7.0) when necessary. The pulp slurry is then diluted with deionized water to 0.5 to 1.0% consistency, filtered and washed with deionized water. Unless otherwise specified, the filtered pulp is diluted with deionized water, stirred and filtered two more times.

General Procedure C Employed in the Examples: Reaction in an Alkaline Peroxide Bleaching Medium

Prior to bleaching, the mechanical wood pulp is treated/chelated with a chelating agent such as diethylenetriaminopentaacetic acid, pentasodium salt (DTPA- Na_5) (0.2-0.6%) at 50 °C, pH 5-6 and 2% consistency for 30 minutes to remove metal ions [Ali *et al. J. Pulp Paper Sci.*, 12(6): J166-172, 1986]. Alternatively, the chelating agent is added directly to the bleaching of the pulps, thus eliminating the pretreatment stage. Chelated or unchelated mechanical pulp (normally 12 g OD) is mixed in a Hobart mixer with a known amount of magnesium sulfate, sodium silicate, sodium hydroxide, hydrogen peroxide, a chelating agent (for unchelated pulp), a fibre-reactive yellowing inhibitor or HALS (0.01 - 2.0% on pulp) and deionized water to give a pulp of desired consistency (5.0 - 40%). For bleaching at a temperature < 100 °C, the pulp is then transferred to a polyethylene bag, sealed, and immersed in a hot water bath set at a known

temperature ($> 20^{\circ}\text{C}$, $< 100^{\circ}\text{C}$) for a known bleaching time with occasional manual mixing. For bleaching at $\geq 100^{\circ}\text{C}$, the pulp is placed in a pyrex beaker, covered with a watch glass and heated in an autoclave oven set at a known temperature ($100 - 120^{\circ}\text{C}$) for a known bleaching time. At the end of bleaching, the pulp, either in the bag or in the beaker is cooled in a cold water bath to room temperature ($\sim 20^{\circ}\text{C}$). The pulp is diluted with deionized water, unless otherwise specified, to a consistency of 0.25 to 1.0%. The pH of the pulp slurry is adjusted to 6.5 by addition of 6% aqueous sulfur dioxide solution or 1N sulfuric acid. The pulp is filtered with recycling of the filtrate to recover fines, and washed thoroughly with deionized water, unless otherwise specified.

Nitrogen Content Analysis and Light-Induced Yellowing Experiment

Handsheets of an inhibitor or HALS-reacted bleached mechanical wood pulp and the original (control) pulp are prepared according to CPPA Test Method, Standard C.5, respectively. Total nitrogen contents of the sheets are measured on selected samples according to TAPPI Test Methods, T418 om-90. Accelerated light-induced yellowing experiments of the sheets are performed in a light box (LuzChem Res. Inc.) equipped with 8 F8T5CW fluorescent lamps (Albrite Lighting Ltd.) in a constant 23°C and 50% humidity room. Unless otherwise specified, the light intensity inside the light box is measured to be 1950 ± 20 foot-candle. Ambient office light exposures of selected handsheets are carried out by placing the handsheet samples on a laboratory bench under normal cool-white fluorescent office lights at a normal distance of about six feet with the lights being on 24 hours a day. Unless otherwise specified, the light intensity for such ambient fluorescent office light is measured to be 145 ± 2 foot-candle. Measurements of the % ISO brightness of the samples on a Technibrite

Micro TB-1C instrument according to TAPPI Test Methods, T 452 om-92, are done at different time intervals and converted to post color number (PC number).

5 PC number is defined as follows:

$$PC = [(k/s)_{\text{after}} - (k/s)_{\text{before}}] \times 100$$

$$k/s = (1 - R_{\text{inf}})^2 / 2 R_{\text{inf}}$$

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where k and s are the absorption and scattering coefficients, respectively, and R_{inf} is the value of ISO brightness. The relationship between R_{inf} and the chromophore concentration is non-linear while the PC number is roughly linear to the concentration of the chromophore. The lower the PC
15 number is, the less yellow (brighter) the sample.

EXAMPLE 1

Spruce peroxide-bleached TMP (BTMP) pulps (ISO brightness 75.2 %, total nitrogen content = 0.05% on pulp) were treated with the H₂O-
20 soluble 4-hydroxy-TEMPO (2.0% OD pulp) and 4-amino-TEMPO (2.0% OD pulp), respectively, at 60 °C and pH 9.5 according to the general procedure A disclosed above. Table 1 lists the PC numbers of the original BTMP, the BTMP pulps treated with 4-hydroxy-TEMPO and 4-amino-TEMPO, respectively, versus the accelerated light exposure times.
25 Treatment with 4-amino-TEMPO greatly improves the brightness stability of the BTMP pulp while treatment with 4-hydroxy-TEMPO does not improve the brightness stability of the pulp. The total nitrogen contents of the 4-hydroxy-TEMPO treated and 4-amino-TEMPO treated BTMP pulps are 0.04% and 0.16% (on pulp), respectively, which correspond to an

attachment of 0.0% (on pulp) of 4-hydroxy-TEMPO and 0.67% (on pulp) of 4-amino-TEMPO to the BTMP pulps.

TABLE 1

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-hydroxy-TEMPO	BTMP treated with 4-amino-TEMPO
0	0.0	0.0	0.0
6	1.8	2.0	0.6
24	4.4	4.8	1.4
48	7.4	8.1	2.3
72	10.1	11.0	3.3
98	12.7	13.8	4.4
170	19.0	21.0	7.2
218	22.8	25.1	9.0
266	25.8	28.3	10.5
337	30.3	32.9	12.7

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EXAMPLE 2

The same BTMP pulps as the ones used in example 1 were treated with the H₂O-soluble 4-hydroxy-TEMPO (2.0% OD pulp) and 4-amino-TEMPO (2.0% OD pulp), respectively, at room temperature (~ 20 °C) and pH 6.5 – 7.0 according to the general procedure A disclosed. Table 2 lists the PC numbers of the original BTMP, the BTMP pulps treated with 4-hydroxy-TEMPO and 4-amino-TEMPO, respectively, versus the accelerated light exposure times. Again, treatment with 4-amino-TEMPO greatly improves the brightness stability of the BTMP pulp while treatment with 4-hydroxy-TEMPO does not improve the brightness stability of the pulp as seen by inspection of the PC numbers. The total nitrogen contents of the BTMP pulps treated with 4-hydroxy-TEMPO and 4-amino-TEMPO

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are 0.05% and 0.19% (on pulp), respectively, which correspond to an attachment of 0.0% (on pulp) of 4-hydroxy-TEMPO and 0.85% (on pulp) of 4-amino-TEMPO to the BTMP pulps.

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TABLE 2

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-hydroxy-TEMPO	BTMP treated with 4-amino-TEMPO
0	0.0	0.0	0.0
6	1.8	1.9	0.7
24	4.4	4.4	1.6
48	7.4	7.1	2.6
72	10.1	9.7	3.6
98	12.7	12.5	4.7
170	19.0	19.0	7.6
218	22.8	22.9	9.4
266	25.8	26.1	11.0
337	30.3	30.4	13.1

EXAMPLE 3

The same BTMP pulps as the ones used in example 1 were treated with the H₂O-soluble 4-amino-TEMPO at a charge of 2.0% and 1.0% (OD pulp), respectively, at room temperature (~ 20 °C) and pH 6.5 – 7.0 according to the general procedure A disclosed. Table 3 lists the PC numbers of the original BTMP and the two 4-amino-TEMPO treated BTMP pulps versus the accelerated light exposure times. Treatment with 4-amino-TEMPO at a charge of 1.0% (OD pulp) is nearly as effective as treatment with 4-amino-TEMPO at a charge of 2.0% (OD pulp) in improving the brightness stability of the pulps. The total nitrogen contents of the BTMP pulps treated with 2.0% and 1.0% of 4-amino-TEMPO are 0.19% and

0.15% (on pulp), respectively, which correspond to an attachment of 0.85% and 0.61% (on pulp) of 4-amino-TEMPO to the BTMP pulps.

TABLE 3

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-amino-TEMPO (2%)	BTMP treated with 4-amino-TEMPO (1%)
0	0.0	0.0	0.0
6	1.8	0.7	0.8
24	4.4	1.6	1.7
48	7.4	2.6	2.8
72	10.1	3.6	3.9
98	12.7	4.7	5.0
170	19.0	7.6	8.0
218	22.8	9.4	9.9
266	25.8	11.0	11.7
337	30.3	13.1	14.0

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EXAMPLE 4

A spruce BTMP pulp (ISO brightness 76.2%) was reacted with 1.0% (OD pulp) of 4-amino-TEMPO at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed. It was also used to prepare a handsheet and then coated with 1% (OD pulp) of 4-amino-TEMPO. Table 4 shows the PC numbers as well as the ISO brightness values of the original BTMP handsheet, the BTMP handsheet coated with 4-amino-TEMPO and the handsheet of the BTMP reacted with 4-amino-TEMPO versus the accelerated light exposure times, respectively. Reaction of the pulp with 4-amino-TEMPO not only gives a handsheet with similar brightness stabilization to that coated with 4-amino-TEMPO, but also provides the pulp/handsheet with a much higher initial brightness than the sheet coated with 4-amino-TEMPO.

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TABLE 4

PC Number [ISO brightness] of the BTMP Pulps versus Accelerated Light Exposure Time			
Time (h)	BTMP	BTMP coated with 4-amino-TEMPO	BTMP reacted with 4-amino-TEMPO
0	0.0 [76.2%]	0.0 [69.1%]	0.0 [74.3%]
6	1.8 [72.0%]	1.0 [67.4%]	0.6 [72.8%]
24	4.7 [66.6%]	2.4 [65.2%]	1.5 [71.0%]
48	7.3 [62.8%]	3.7 [63.3%]	2.4 [69.2%]
72	10.1 [59.5%]	4.9 [61.8%]	3.5 [67.3%]
96	12.5 [57.0%]	5.8 [60.7%]	4.4 [65.8%]
168	19.2 [51.5%]	8.1 [58.2%]	7.3 [61.9%]
216	22.7 [49.1%]	9.3 [57.0%]	9.0 [59.9%]
264	26.0 [47.1%]	10.5 [55.9%]	10.7 [58.1%]

EXAMPLE 5

5 The same BTMP pulp as the ones used in example 1 was treated with the H₂O-soluble 4-amino-TEMPO at a charge of 1.0% (OD pulp) at room temperature (~ 20 °C) and pH 6.5 – 7.0 according to the general procedure A disclosed. The treated pulp was divided into two equivalent portions. One portion of the pulp was further treated with ascorbic acid

10 (1% OD. pulp) at room temperature (~ 20 °C) for one hour at 1.5% consistency. Table 5 lists the PC numbers and the ISO brightness values of the original BTMP, the 4-amino-TEMPO treated BTMP pulp, and the 4-amino-TEMPO and ascorbic acid treated BTMP pulp versus the accelerated light exposure times. Sequential treatment with 4-amino-TEMPO and

15 ascorbic acid not only gives a pulp with much improved brightness stability but also provides a pulp with initial brightness similar to the control pulp. The total nitrogen contents of both the 4-amino-TEMPO treated BTMP and the 4-amino-TEMPO, ascorbic acid treated BTMP are 0.15% (on pulp),

which correspond to an attachment of 0.61% (on pulp) of 4-amino-TEMPO to both the BTMP pulps.

TABLE 5

PC Number [ISO brightness] of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-amino-TEMPO	BTMP treated with 4-amino-TEMPO and ascorbic acid
0	0.0 [75.2%]	0.0 [73.6%]	0.0 [75.0%]
6	1.8 [71.0%]	0.8 [71.9%]	0.8 [73.0%]
24	4.4 [66.4%]	1.7 [70.0%]	1.8 [70.9%]
48	7.4 [62.2%]	2.8 [68.0%]	2.9 [68.8%]
72	10.1 [59.1%]	3.9 [66.2%]	3.9 [67.1%]
98	12.7 [56.5%]	5.0 [64.5%]	5.0 [65.4%]
170	19.0 [51.3%]	8.0 [60.7%]	8.0 [61.4%]
218	22.8 [48.8%]	9.9 [58.6%]	9.8 [59.3%]
266	25.8 [47.0%]	11.7 [56.8%]	11.5 [57.5%]
337	30.3 [44.6%]	14.0 [54.7%]	13.8 [55.4%]

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EXAMPLE 6

Spruce peroxide-bleached TMP (BTMP) pulps (ISO brightness 76.4 %, total nitrogen content = 0.046% on pulp) were treated with 1.0% (OD pulp) of 4-amino-TEMPO at room temperature (~ 20 °C) and at pH 6.5 - 7.0 and 5.5 - 6.0, respectively, according to the general procedure A disclosed. Table 6 shows the PC numbers as well as the ISO brightness of the original BTMP and the two 4-amino-TEMPO treated BTMP pulps versus the accelerated light exposure times. Treatment of the bleached TMP pulps with 4-amino-TEMPO at pH 5.5-6.0 is also effective in greatly improving the brightness stability of the pulps. It is also effective in

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improving the initial brightness of the BTMP pulp treated with 4-amino-TEMPO.

TABLE 6

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-amino-TEMPO pH 6.5 – 7.0	BTMP treated with 4-amino-TEMPO pH 5.5 – 6.0
0	0.0 [76.4%]	0.0 [74.6%]	0.0 [75.1%]
6	1.9 [71.8%]	0.7 [72.9%]	0.8 [73.1%]
24	4.9 [66.3%]	1.5 [71.1%]	1.6 [71.3%]
48	7.9 [62.1%]	2.6 [69.1%]	2.7 [69.3%]
72	10.6 [59.0%]	3.6 [67.3%]	3.7 [67.5%]
96	13.1 [56.5%]	4.6 [65.8%]	4.9 [65.6%]
168	19.2 [51.5%]	7.3 [62.0%]	7.9 [61.5%]
216	22.7 [49.1%]	9.3 [59.7%]	10.0 [59.1%]
264	26.1 [47.1%]	11.0 [57.9%]	11.9 [57.2%]
336	30.4 [44.8%]	13.3 [55.7%]	14.4 [54.9%]

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EXAMPLE 7

The same BTMP pulps as the one used in example 5 were treated with 1.0% (OD pulp) of 4-amino-TEMPO at 60 °C and pH 6.5-7.0, and at room temperature (~ 20 °C) and pH 6.5 - 7.0 without purging the pulp slurry with N₂ (i.e. in the presence of air/O₂), respectively, according to the general procedure A disclosed. Table 7 lists the PC numbers of the original BTMP and the two 4-amino-TEMPO treated BTMP pulps versus the accelerated light exposure times. Treatment of the bleached TMP pulp with 4-amino-TEMPO at 60 °C or in the presence of air/oxygen is also effective in greatly improving the brightness stability of the pulp.

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TABLE 7.

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP treated with 4-amino-TEMPO at 60 °C with N ₂ purging	BTMP treated with 4-amino-TEMPO at ~ 20 °C without N ₂ purging
0	0.0	0.0	0.0
6	1.9	0.7	0.8
24	4.9	1.7	1.6
48	7.9	2.8	2.8
72	10.6	4.0	3.8
96	13.1	5.0	4.9
168	19.2	8.4	7.9
216	22.7	10.3	9.7
264	26.1	12.3	11.7
336	30.4	14.9	14.1

EXAMPLE 8

Spruce BTMP pulps (ISO brightness 76.4% or 75.5%, total nitrogen content = 0.046%) were reacted with 1.0% and 0.2% (OD pulp) of 4-amino-TEMPO, respectively, at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed. Tables 8.1 and 8.2 show the PC numbers as well as the ISO brightness values of the BTMP and the 4-amino-TEMPO reacted BTMP pulps versus the accelerated and ambient office light exposure times, respectively. The brightness stability of the BTMP pulps can be dramatically improved by reaction with 1.0% or 0.2% (OD pulp) of 4-amino-TEMPO, particularly when the pulps are exposed to ambient light. The total nitrogen contents of the BTMP pulps reacted with 1.0% and 0.2% of 4-amino-TEMPO are 0.140% and 0.073% (on pulp), respectively, which correspond to an attachment of 0.57% and 0.16% (on pulp) of 4-amino-TEMPO to the BTMP pulps. Data of the PC numbers and ISO brightness values versus ambient light exposure times for the control

BTMP pulp and the BTMP pulps reacted with 4-amino-TEMPO are shown in Figures 1 and 2, respectively.

TABLE 8.1

PC Number [ISO Brightness] of the BTMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP	BTMP reacted with 4-amino-TEMPO (1%)	BTMP reacted with 4-amino-TEMPO (0.2%)
0	0.0 [76.4%]	0.0 [74.6%]	0.0 [76.0%]
6	1.9 [71.8%]	0.7 [72.9%]	1.2 [73.0%]
24	4.9 [66.3%]	1.5 [71.1%]	2.6 [70.0%]
48	7.9 [62.1%]	2.6 [69.1%]	4.2 [67.2%]
72	10.6 [59.0%]	3.6 [67.3%]	6.1 [64.4%]
96	13.1 [56.5%]	4.6 [65.8%]	7.8 [62.1%]
168	19.2 [51.5%]	7.3 [62.0%]	12.4 [57.0%]
216	22.7 [49.1%]	9.3 [59.7%]	15.3 [54.4%]
264	26.1 [47.1%]	11.0 [57.9%]	17.8 [52.4%]
336	30.4 [44.8%]	13.3 [55.7%]	21.2 [50.0%]

TABLE 8.2

PC Number [ISO Brightness] of the BTMP Pulps versus Ambient Light Exposure Time (days)			
Time (d)	BTMP	BTMP reacted with 4-amino-TEMPO (1%)	BTMP reacted with 4-amino-TEMPO (0.2%)
0	0.0 [75.5%]	0.0 [73.9%]	0.0 [75.8%]
1	0.4 [74.5%]	-0.1 [74.1%]	0.1 [75.5%]
2	0.8 [73.6%]	0.0 [74.0%]	0.2 [75.2%]
3	1.1 [72.9%]	0.0 [73.8%]	0.3 [74.9%]
4	1.4 [72.1%]	0.1 [73.6%]	0.5 [74.6%]
7	2.3 [70.3%]	0.3 [73.2%]	0.8 [73.8%]
9	2.9 [69.1%]	0.5 [72.8%]	1.0 [72.8%]
11	3.6 [68.0%]	0.6 [72.1%]	1.2 [72.1%]
14	4.3 [66.7%]	0.8 [71.9%]	1.5 [71.9%]
17	5.3 [65.2%]	1.1 [71.5%]	1.9 [71.3%]
20	6.3 [63.8%]	1.3 [71.1%]	2.3 [70.5%]
22	6.9 [63.0%]	1.4 [70.8%]	2.6 [70.0%]
24	7.4 [62.3%]	1.6 [70.5%]	2.8 [69.5%]
27	8.3 [61.2%]	1.8 [70.1%]	3.2 [68.9%]
29	9.0 [60.4%]	1.9 [69.8%]	3.4 [68.4%]
31	9.5 [59.8%]	2.0 [69.6%]	3.8 [67.8%]
34	10.5 [58.8%]	2.2 [69.2%]	4.1 [67.2%]
36	11.0 [58.2%]	2.4 [68.9%]	4.4 [66.7%]
38	11.6 [57.6%]	2.6 [68.6%]	4.8 [66.2%]
43	13.1 [56.2%]	2.9 [68.0%]	5.5 [65.1%]
45	13.6 [55.7%]	3.1 [67.7%]	5.8 [64.7%]
48	14.4 [55.0%]	3.3 [67.4%]	6.3 [64.0%]
50	14.9 [54.6%]	3.4 [67.2%]	6.6 [63.6%]
52	15.6 [54.0%]	3.6 [66.9%]	6.9 [63.2%]
56	16.7 [53.1%]	3.8 [66.5%]	7.5 [62.4%]
57	17.0 [52.9%]	3.9 [66.4%]	7.6 [66.4%]
59	17.6 [52.4%]	4.1 [66.0%]	7.9 [61.8%]
62	18.4 [51.8%]	4.3 [65.8%]	8.4 [61.3%]
64	18.9 [51.5%]	4.5 [65.5%]	8.8 [60.8%]
66	19.4 [51.1%]	4.7 [65.2%]	9.1 [60.4%]
69	20.0 [50.7%]	4.8 [65.0%]	9.5 [59.9%]
71	20.5 [50.3%]	5.0 [64.7%]	9.8 [59.6%]

EXAMPLE 9

The same BTMP pulp as the ones used in example 6 was treated with 1.0% (OD pulp) of 4-amino-TEMPO at room temperature and pH 5.5 - 6.0 according to the general procedure A disclosed. Handsheets of the 4-amino-TEMPO treated pulp and the original (control) pulp were then coated with 1% (OD pulp) of an ultraviolet absorber, the sodium salt of 2-(3'-sulfo-5'-sec-butyl-6'-hydroxyphenyl)benzotriazole (Cibafast W) dissolved in ethanol. Table 9 shows the PC numbers of the original BTMP, the original BTMP coated with the UVA, the 4-amino-TEMPO treated BTMP, and the 4-amino-TEMPO treated BTMP coated with the UVA versus the accelerated light exposure times, respectively. A nearly complete brightness stabilization of the BTMP pulp can be achieved by reaction of the pulp with 4-amino-TEMPO and then by coating the sheet made from the 4-amino-TEMPO-reacted pulp with the UVA.

TABLE 9

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)				
Time (h)	BTMP	BTMP coated with UVA	BTMP reacted with 4-amino-TEMPO	BTMP reacted with 4-amino-TEMPO and coated with UVA
0	0.0	0.0	0.0	0.0
6	1.9	1.0	0.8	0.3
24	4.3	2.4	1.5	0.5
48	7.0	4.1	2.5	0.9
72	9.5	5.6	3.4	1.2
96	12.1	7.1	4.3	1.5
144	16.4	10.0	6.5	2.2
168	18.4	11.4	7.6	2.5
192	20.2	12.9	8.6	3.1
216	22.0	14.0	9.6	3.4
240	23.5	15.3	10.6	3.8

EXAMPLE 10

The same BTMP pulps as the ones used in example 6 were treated with 1.0% (OD pulp) of 4-amino-TEMPO at room temperature and pH 5.5 - 6.0 for 0.5 hour according to the general procedure A disclosed, and treated with 1.0% (OD pulp) of 4-amino-TEMPO at 40 °C, and at 5% and 10% consistency (Cs.), respectively, according to the general procedure B disclosed. Table 10 shows the PC numbers of the original BTMP, the three 4-amino-TEMPO treated BTMP pulps versus the accelerated light exposure times, respectively. The reaction of 4-amino-TEMPO with pulps can be carried out at various consistencies for 0.5 or 3 hours to give pulps with much improved brightness stability.

TABLE 10

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)				
Time (h)	BTMP	BTMP treated with 4-amino-TEMPO (1.5% Cs., 0.5 h)	BTMP treated with 4-amino-TEMPO (5% Cs., 3 h)	BTMP treated with 4-amino- TEMPO (10% Cs., 3 h)
0	0.0	0.0	0.0	0.0
6	1.7	0.6	0.7	0.7
24	4.1	1.3	1.6	1.7
48	6.8	2.2	2.7	2.8
96	12.1	4.0	4.7	4.8
168	18.8	6.5	7.6	7.7
216	22.9	8.4	9.5	10.1
264	25.5	9.9	11.1	12.1
336	29.8	12.0	13.4	14.8

EXAMPLE 11

A spruce BTMP pulp (total nitrogen content = 0.034% on pulp) was
 5 treated with 1.0% (OD pulp) of 3-amino-2,2,5,5-tetramethyl-1-
 pyrrolidinyloxy (formula B where $R_1 = H$, $R_2 = R_3 = R_4 = R_5 = CH_3$ and Y
 = oxyl), 3-amino-TEMpyrrolidinylo (purchased from Arcos Organics) at
 room temperature and pH 6.5 - 7.0 according to the general procedure A
 disclosed. Table 11 lists the PC numbers and ISO brightness values of the
 10 original BTMP and the BTMP pulp treated with 3-amino-
 TEMpyrrolidinylo versus the accelerated light (light intensity = 1940 ∇ 40
 foot-candle) exposure times. Treatment of the pulp with 3-amino-
 TEMpyrrolidinylo provides a noticeable improvement of brightness
 stability to the pulp. The total nitrogen content of the BTMP pulp treated
 15 with 3-amino-TEMpyrrolidinylo is 0.078% (on pulp), respectively, which

corresponds to an attachment of 0.25% (on pulp) of the inhibitor to the BTMP pulp.

TABLE 11

PC Number [ISO Brightness] of the BTMP Pulps versus Accelerated Light Exposure Time (hours)		
Time (h)	BTMP	BTMP treated with 3-amino-TEMpyrrolidinylO
0	0.0 [76.6%]	0.0 [75.9%]
6	1.9 [72.0%]	1.0 [73.4%]
24	4.9 [66.4%]	2.9 [69.5%]
48	7.9 [62.2%]	5.3 [65.5%]
72	10.6 [59.1%]	7.5 [62.4%]
144	17.5 [52.8%]	14.0 [55.5%]
192	21.4 [50.0%]	18.1 [52.2%]
240	25.1 [47.7%]	21.6 [49.7%]
336	30.8 [44.6%]	27.7 [46.1%]

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EXAMPLE 12

Spruce BTMP pulps (total nitrogen content = 0.032% on pulp) were treated with 1.0% and 0.5% (OD pulp) of 1-hydroxyl-4-amino-2,2,6,6-tetramethylpiperidine dihydrochloride (formula C where $R_1 = H$, $R_2 = R_3 = R_4 = R_5 = CH_3$, $X = Cl$, $m = k = 1$ and $p = 2$), 4-amino-TEMPOH-2HCl, prepared from the reaction of 4-amino-TEMPO and hydrochloric acid in ethanol according to a literature procedure [Sosnovsky and Cai, *J. Org. Chem.* **60**: 3414-3418, 1995], at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed. The same spruce BTMP pulp is also treated with 0.5% (OD pulp) of 4-amino-TEMPOH-2HCl at 40 °C and 20% consistency according to the general procedure B disclosed. Table 12 lists the PC numbers as well as the ISO brightness values of the original BTMP and the three treated BTMP pulps versus the accelerated

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light (light intensity = 1950 ∇ 80 foot-candle) exposure times. The BTMP pulps treated with 4-amino-TEMPOH-2HCl have slightly higher initial brightness and much higher brightness stability than the control pulp. The total nitrogen contents of the three treated BTMP pulps are 0.112%, 0.082% and 0.078% (on pulp), respectively, which correspond to an attachment of 0.70%, 0.44%, and 0.40% (on pulp) of the inhibitor to the BTMP pulps, respectively.

TABLE 12

PC Number [ISO Brightness] of the BTMP Pulps versus Accelerated Light Exposure Time (h)				
Time (h)	BTMP	BTMP treated with 4-amino-TEMPOH-2HCl (1.0%, 1.5% Cs.)	BTMP treated with 4-amino-TEMPOH-2HCl (0.5%, 1.5% Cs.)	BTMP treated with 4-amino-TEMPOH-2HCl (0.5%, 20% Cs.)
0	0.0 [76.1%]	0.0 [76.3%]	0.0 [76.7%]	0.0 [76.8%]
6	1.8 [71.8%]	0.7 [74.4%]	0.8 [74.6%]	1.0 [74.2%]
24	4.5 [66.8%]	1.6 [72.3%]	1.9 [72.0%]	2.3 [71.3%]
72	9.6 [60.0%]	3.6 [68.4%]	4.7 [66.8%]	5.3 [65.9%]
144	16.7 [53.3%]	6.7 [63.7%]	9.0 [60.9%]	10.1 [59.7%]
192	20.4 [50.6%]	8.6 [61.2%]	11.5 [58.2%]	12.8 [56.9%]
240	23.9 [48.3%]	10.4 [59.2%]	13.7 [56.0%]	15.3 [54.7%]
312	27.9 [46.0%]	12.7 [56.8%]	16.7 [53.5%]	18.4 [52.2%]

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EXAMPLE 13

The same BTMP pulps as the ones used in example 12 were treated with 1.0% (OD pulp) of 1-hydroxyl-4-amino-2,2,6,6-tetramethylpiperidine sulfuric acid salt, 4-amino-TEMPOH-SA, and 1-hydroxyl-4-amino-2,2,6,6-tetramethylpiperidine citric acid salt, 4-amino-TEMPOH-CA, both prepared

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from the reaction of 4-amino-TEMPO and the corresponding acids in ethanol according to a literature procedure [Sosnovsky and Cai, *J. Org. Chem.* **60**: 3414-3418, 1995], respectively, at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed. They were also
 5 treated with 4-amino-TEMPOH-CA and 4-amino-TEMPOH-2HCl, respectively, at room temperature and pH 6.5 - 7.0 for 10 minutes according to the general procedure A disclosed. Table 13 lists the PC numbers of the original BTMP and the BTMP pulps treated with the said inhibitors versus
 10 the accelerated light (light intensity = 1880 ∇ 40 foot-candle) exposure times. Treatment of the pulps with 4-amino-TEMPOH-SA, 4-amino-TEMPOH-CA or 4-amino-TEMPOH-2HCl for 3 hours or 10 minutes provides the pulps with much improved brightness stability.

TABLE 13

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)					
Time (h)	BTMP	SA salt (3 h)	CA salt (3 h)	CA salt (10 min)	4-amino-TEMPOH-2HCl (10 min)
0	0.0	0.0	0.0	0.0	0.0
6	1.5	1.1	0.6	0.6	0.4
24	4.0	2.6	1.7	1.6	1.1
48	6.4	4.0	2.9	3.0	1.9
96	11.2	6.7	5.6	5.9	3.7
216	21.0	12.7	11.9	12.7	8.0
264	24.3	14.9	14.3	15.3	9.7

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EXAMPLE 14

A chelated spruce TMP pulps were bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃ and 0.05% Mg, (as MgSO₄) at 60 °C and 10 or 20% consistency in the absence (0.0%) and in the presence of 0.5% (OD pulp) of

4-amino-TEMPO or 1.0% (OD pulp) of 4-amino-TEMPOH-2HCl, respectively, according to the general procedure C disclosed. Table 14 lists the PC numbers of the control BTMP (bleached in the absence of 4-amino-TEMPO or 4-amino-TEMPOH-2HCl) and the BTMP pulps bleached in the presence of 4-amino-TEMPO or 4-amino-TEMPOH-2HCl versus the accelerated light (light intensity = 1850 W.25) exposure times, respectively. Addition of 4-amino-TEMPO or 4-amino-TEMPOH-2HCl to alkaline peroxide bleaching of the pulps allows both the reaction of the fibre-reactive yellowing inhibitors with the pulps and the bleaching of the pulps to occur at the same time to give bleached pulps with much improved brightness stability.

TABLE 14

PC Number of the Bleached TMP Pulps versus Accelerated Light Exposure Time (hours)			
Time (h)	BTMP (20% Cs.)	BTMP bleached in the presence of 4-amino-TEMPO (0.5%) (10% Cs.)	BTMP bleached in the presence of 4-amino-TEMPOH-2HCl (1.0%) (20% Cs.)
0	0.0	0.0	0.0
6	1.8	1.0	0.9
24	4.4	2.4	2.4
48	7.0	4.2	3.7
96	11.9	7.9	6.4
216	21.5	16.1	12.4
264	24.7	18.8	14.6

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EXAMPLE 15

An aspen unbleached CTMP and an aspen peroxide-bleached CTMP (BCTMP) were reacted, respectively, with 1.0% (OD pulp) of 4-amino-

TEMPOH-2HCl at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed except without purging the pulp slurries with N₂. Table 15 lists the PC numbers as well as the ISO brightness values of the original CTMP and BCTMP pulps, and the CTMP and BCTMP pulps treated with 4-amino-TEMPOH-2HCl versus the accelerated light (light intensity = 1936 ∇ 20 foot-candle) exposure times. Treatment of both the CTMP and BCTMP pulps with 4-amino-TEMPOH-2HCl provides the pulps with much improved brightness stability as well as slightly higher initial brightness values.

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TABLE 15

PC Number [ISO brightness] of the Unbleached and Bleached Aspen CTMP Pulps versus Accelerated Light Exposure Time (hours)				
Time (h)	CTMP	CTMP treated with 4-amino-TEMPOH-2HCl	BCTMP	CTMP treated with 4-amino-TEMPOH-2HCl
0	0.0 [67.9%]	0.0 [68.6%]	0.0 [79.3%]	0.0 [79.7%]
24	1.9 [64.9%]	0.6 [67.6%]	2.8 [72.0%]	1.3 [75.7%]
48	3.0 [63.4%]	1.1 [66.7%]	4.5 [68.7%]	2.0 [73.9%]
96	5.3 [60.6%]	2.1 [65.1%]	7.6 [63.8%]	3.3 [71.0%]
168	8.4 [57.2%]	3.7 [62.9%]	11.7 [58.9%]	5.1 [67.7%]
216	10.2 [55.5%]	4.7 [61.7%]	14.0 [56.5%]	6.2 [66.0%]
264	12.0 [54.0%]	5.9 [60.3%]	16.4 [54.4%]	7.4 [64.2%]
336	14.4 [52.1%]	7.4 [58.7%]	19.6 [51.9%]	9.0 [62.1%]

EXAMPLE 16

Spruce BTMP pulps (total nitrogen content = 0.037% on pulp) were treated with 0.5% and 0.1% (OD pulp) of 4-amino-TEMPO, respectively, at room temperature and pH 6.5-7.0 according to the general procedure A disclosed. Table 16 lists the PC numbers as well as the ISO brightness

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values of the original BTMP and the two BTMP pulps treated with 4-amino-TEMPO versus some of the ambient office light (light intensity = 145 ∇ 10 foot-candle) exposure times. The brightness stability of the BTMP pulp can be dramatically improved by treatment with 0.5% (OD pulp) of 4-amino-TEMPO, and significantly improved with 0.1% (OD pulp) of 4-amino-TEMPO. The total nitrogen contents of the BTMP pulps treated with 0.5% and 0.1% of 4-amino-TEMPO are 0.103% and 0.052% (on pulp), respectively, which correspond to an attachment of 0.40% and 0.09% (on pulp) of 4-amino-TEMPO to the BTMP pulps, respectively.

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Table 16

PC Number [ISO brightness] of the BTMP pulps versus Ambient Light Exposure Time (days)			
Time (d)	BTMP	BTMP treated with 4-amino-TEMPO (0.5%)	BTMP treated with 4-amino-TEMPO (0.1%)
0	0.0 [76.2%]	0.0 [75.1%]	0.0 [76.2%]
8	2.7 [70.0%]	0.5 [73.9%]	1.2 [73.2%]
14	4.5 [66.8%]	1.0 [72.7%]	2.2 [71.1%]
21	6.5 [63.9%]	1.7 [71.3%]	3.2 [69.0%]
28	8.4 [61.4%]	2.3 [70.0%]	4.4 [67.0%]
39	11.4 [58.1%]	3.4 [68.0%]	6.4 [64.1%]
49	14.1 [55.5%]	4.6 [66.1%]	8.2 [61.7%]
58	16.8 [53.3%]	5.8 [64.2%]	10.3 [59.3%]
70	20.1 [50.8%]	7.4 [62.2%]	12.7 [56.8%]
81	22.5 [49.2%]	8.7 [60.6%]	14.6 [55.1%]
92	25.2 [47.6%]	10.1 [59.0%]	16.9 [53.2%]

EXAMPLE 17

An aspen BCTMP pulp obtained from a Western Canadian pulp mill and a laboratory bleached, mixed (black spruce/pine/fir) softwood

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groundwood pulp (GWP) obtained from an Eastern Canadian pulp mill were reacted with 0.5% (OD pulp) of 4-amino-TEMPOH-2HCl at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed except without purging the pulp slurries with N₂. Table 17 lists the PC numbers as well as the ISO brightness values of the original BCTMP and the bleached GWP (BGWP) pulps, and the BCTMP and BGWP pulps treated with 4-amino-TEMPOH-2HCl versus some of the ambient office light (light intensity = 84 \forall 5 foot-candle) exposure times. Treatment of both the BCTMP and BGWP pulps with 4-amino-TEMPOH-2HCl provides the pulps with much improved brightness stability.

TABLE 17

PC Number [ISO Brightness] of the Mill Aspen BCTMP Pulps and Mixed Softwood BGWP Pulps versus Ambient Light Exposure Time (days)				
Time (d)	BCTMP	BCTMP treated with 4-amino-TEMPOH-2HCl	BGWP	BGWP treated with 4-amino-TEMPOH-2HCl
0	0.0 [82.4%]	0.0 [82.5%]	0.0 [80.6%]	0.0 [80.9%]
7	0.6 [80.0%]	0.3 [81.1%]	1.1 [77.1%]	0.3 [79.8%]
14	1.1 [78.3%]	0.6 [80.1%]	2.1 [74.5%]	0.6 [78.8%]
21	1.6 [76.8%]	0.9 [79.2%]	3.1 [72.0%]	0.9 [77.8%]
28	2.1 [75.5%]	1.1 [78.6%]	4.1 [70.0%]	1.2 [77.0%]
49	3.7 [71.8%]	1.7 [76.7%]	7.2 [64.9%]	2.0 [74.8%]
84	6.6 [66.4%]	2.8 [73.7%]	12.6 [58.3%]	3.6 [71.1%]
91	7.3 [65.3%]	3.2 [72.9%]	13.6 [57.2%]	3.9 [70.6%]

EXAMPLE 18

An aspen BCTMP pulp (ISO brightness 80.8%) was treated with 1.0% (OD pulp) of 4-amino-TEMPOH-2HCl at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed except without

purging the pulp slurry with N_2 . Various amounts of the original BCTMP and the 4-amino-TEMPOH-2HCl treated BCTMP pulps were blended, respectively, with a fully bleached aspen kraft pulp (ISO brightness = 86.5%) to give fully bleached aspen kraft pulps containing various amounts of the BCTMP or the 4-amino-TEMPOH-2HCl treated BCTMP. Table 18 lists the PC numbers as well as brightness values of four of the blended pulps versus some of the ambient light (light intensity = 79 \pm 7 foot-candle) exposure times. Fully bleached kraft pulps containing, for example 20% of the 4-amino-TEMPOH-2HCl treated BCTMP pulps have much higher brightness stability than those containing same amounts of the untreated BCTMP pulps. A much higher portion (e.g. 40%) of the treated BCTMP pulps than untreated BCTMP pulps (e.g. 10%) can be combined with fully bleached kraft pulps to give blended pulps with similar brightness stability.

TABLE 18

PC Number [ISO Brightness] of Fully Bleached Aspen Kraft Pulps Containing Various Amounts of Aspen BCTMP Pulps versus Ambient Light Exposure Time (days)				
Time (d)	10% BCTMP	20% BCTMP	20% treated BCTMP	40% treated BCTMP
0	0.0 [86.1%]	0.0 [85.7%]	0.0 [85.6%]	0.0 [84.8%]
5	0.3 [84.7%]	0.3 [84.0%]	0.2 [84.4%]	0.3 [83.5%]
9	0.4 [84.1%]	0.5 [83.2%]	0.3 [84.0%]	0.4 [83.0%]
20	0.7 [82.7%]	1.0 [81.2%]	0.6 [82.8%]	0.7 [81.7%]
30	0.9 [81.7%]	1.4 [79.8%]	0.8 [82.0%]	0.9 [80.8%]
40	1.1 [80.9%]	1.7 [78.6%]	0.9 [81.4%]	1.1 [80.1%]
49	1.4 [80.0%]	2.1 [77.5%]	1.1 [80.7%]	1.3 [79.4%]
58	1.5 [79.5%]	2.4 [76.6%]	1.3 [80.1%]	1.5 [78.9%]
68	1.8 [78.7%]	2.7 [75.6%]	1.5 [79.4%]	1.7 [78.2%]
79	2.0 [77.9%]	3.2 [74.5%]	1.7 [78.7%]	1.9 [77.5%]
91	2.3 [77.1%]	3.6 [73.5%]	1.9 [78.0%]	2.1 [76.8%]

EXAMPLE 19

A chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and, 0.0% (control) and 1.0% (OD pulp) of 4-amino-2,2,6,6-tetramethylpiperidine, respectively, at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. Table 19 lists the ISO brightness values as well as the PC numbers of the two BTMP pulps versus the ambient light exposure times, respectively.

Data of the ISO brightness values and the PC numbers versus the ambient light (light intensity = 85 ± 3 foot-candle) exposure times of the pulps are given in Figures 3 and 4, respectively. Bleaching of the pulp in the

presence of 4-amino-2,2,6,6-tetramethylpiperidine gives a bleached pulp with much improved brightness stability.

TABLE 19

PC Number [ISO Brightness] of the BTMP Pulps versus Ambient Light Exposure Time (days)		
Time (d)	BTMP (control)	BTMP bleached in the presence of 4-amino- 2,2,6,6-tetramethylpiperidine
0	0.0 [75.9%]	0.0 [75.4%]
2	0.5 [74.7%]	0.0 [75.5%]
5	1.1 [73.2%]	0.1 [75.1%]
9	1.8 [71.6%]	0.4 [74.5%]
12	2.4 [70.5%]	0.6 [74.0%]
14	2.8 [69.7%]	0.7 [73.7%]
16	3.1 [69.0%]	0.8 [73.3%]
21	4.1 [67.3%]	1.1 [72.7%]
23	4.6 [66.5%]	1.3 [72.3%]
26	5.2 [65.7%]	1.6 [71.7%]
28	5.2 [65.6%]	1.9 [71.0%]
30	5.9 [64.6%]	2.1 [70.6%]
33	6.5 [63.8%]	2.4 [70.1%]
35	6.8 [63.3%]	2.5 [69.8%]
37	7.3 [62.7%]	2.7 [69.5%]
40	7.9 [61.8%]	3.0 [68.9%]
42	8.3 [61.5%]	3.1 [68.7%]
44	8.6 [61.1%]	3.3 [68.4%]
47	9.4 [60.2%]	3.6 [67.8%]
49	9.7 [59.8%]	3.7 [67.7%]
51	10.1 [59.3%]	4.0 [67.2%]
54	10.6 [58.8%]	4.2 [66.9%]
56	11.0 [58.4%]	4.3 [66.6%]
58	11.4 [57.9%]	4.5 [66.3%]
62	12.5 [56.9%]	5.1 [65.5%]
69	13.8 [55.7%]	5.7 [64.6%]
72	14.3 [55.2%]	5.9 [64.4%]
75	14.9 [54.7%]	6.2 [63.9%]
79	15.6 [54.1%]	6.5 [63.5%]
82	16.2 [53.7%]	6.7 [63.1%]
84	16.7 [53.2%]	7.0 [62.8%]
86	16.9 [53.1%]	7.1 [62.6%]

EXAMPLE 20

A chelated spruce TMP was bleached with 5% H_2O_2 , 4% NaOH, 3% Na_2SiO_3 , 0.05% Mg (as $MgSO_4$) and, 0.0% (control), 0.2% and 1.0% (OD pulp) of 4-amino-2,2,6,6-tetramethylpiperidine (abbreviated as amino-HALS hereafter), respectively, at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. A portion of a handsheet made from the control BTMP was coated with 1.0% (OD pulp) of amino-HALS dissolved in deionized water. Table 20 shows the PC numbers of the control BTMP, the control BTMP coated with amino-HALS, the BTMP bleached in the presence of 0.2% and 1.0% (OD pulp) of amino-HALS, respectively, versus the ambient light (light intensity = 85 \pm 3 foot-candle) exposure times. Coating of the BTMP with amino-HALS produces a detrimental effect on the brightness stability of the BTMP sheet, consistent with the results reported in the prior art. However, bleaching of the pulps in the presence of amino-HALS (0.2 or 1.0% on pulp) provides the bleached pulps with much improved brightness stability.

TABLE 20

PC Numbers of the Bleached TMP Pulps versus Ambient Light Exposure Times (days)				
Time (d)	BTMP	BTMP coated with 1.0% amino-HALS	BTMP bleached in the presence of 0.2% amino-HALS	BTMP bleached in the presence of 1.0% amino- HALS
0	0.0	0.0	0.0	0.0
3	0.7	1.0	0.5	0.1
5	1.1	1.6	0.8	0.3
7	1.5	2.1	1.1	0.4
10	2.1	2.8	1.6	0.7
12	2.5	3.2	1.9	0.9
14	2.9	3.7	2.2	1.0
19	4.0	4.8	3.1	1.6
21	4.4	5.2	3.4	1.8
24	5.1	5.9	3.9	2.1
26	5.5	6.3	4.2	2.3
28	5.9	6.6	4.6	2.5
31	6.5	7.2	5.0	2.8
33	6.9	7.5	5.3	3.0
35	7.2	7.7	5.6	3.1
38	7.9	8.2	6.1	3.4
40	8.2	8.4	6.4	3.6

EXAMPLE 21

A chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and 0.0% amino-HALS (control BTMP) at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. The same chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) in the presence of 1.0% (OD pulp) of amino-HALS at 20% consistency and 60 °C, 70 °C and 80 °C, respectively, for 3 hours according to the general procedure C disclosed. Table 21 shows the PC numbers of the control BTMP, the BTMP pulps bleached in the presence of 1.0% (OD pulp) of amino-HALS at various temperatures versus the ambient light (light intensity = 85 ∓ 3 foot-candle) exposure times, respectively. Bleaching of the spruce TMP pulps in the

presence of amino-HALS at various temperatures provides the bleached pulps much improved brightness stability.

TABLE 21

PC Numbers of the BTMP Pulps versus Ambient Light Exposure Times (days)				
Time (d)	BTMP	BTMP bleached in the presence of amino-HALS at 60 °C	BTMP bleached in the presence of amino- HALS at 70 °C	BTMP bleached in the presence of amino-HALS at 80 °C
0	0.0	0.0	0.0	0.0
3	0.7	0.1	0.1	0.1
5	1.1	0.3	0.2	0.2
7	1.5	0.4	0.4	0.4
10	2.1	0.7	0.6	0.5
12	2.5	0.9	0.8	0.7
14	2.9	1.0	0.9	0.8
19	4.0	1.6	1.4	1.2
21	4.4	1.8	1.5	1.4
24	5.1	2.1	1.7	1.6
26	5.5	2.3	1.9	1.7
28	5.9	2.5	2.0	1.8
31	6.5	2.8	2.3	2.1
33	6.9	3.0	2.4	2.2
35	7.2	3.1	2.6	2.4
38	7.9	3.4	2.8	2.7
40	8.2	3.6	3.0	2.8

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EXAMPLE 22

A chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and 0.0% amino-HALS (control BTMP) at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. The same chelated spruce TMP pulps were also bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and with 5% H₂O₂, 5% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄), respectively, in the presence of 1.0% amino-HALS at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. Table 22 shows the PC numbers of the control BTMP, the BTMP bleached in the presence of 1.0%

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amino-HALS at two different NaOH charges versus the ambient light (light intensity = 85 ∇ 3 foot-candle) exposure times, respectively. Bleaching of the spruce TMP pulps in the presence of amino-HALS at two different NaOH charges provides the bleached pulps with much improved brightness stability.

TABLE 22

PC Numbers of the Bleached TMP Pulps versus Ambient Light Exposure Times (days)			
Time (d)	BTMP	BTMP bleached in the presence of amino-HALS (4% NaOH)	BTMP bleached in the presence of amino-HALS (5% NaOH)
0	0.0	0.0	0.0
3	0.7	0.1	0.3
5	1.1	0.3	0.4
7	1.5	0.4	0.7
10	2.1	0.7	1.0
12	2.5	0.9	1.3
14	2.9	1.0	1.5
19	4.0	1.6	2.1
21	4.4	1.8	2.4
24	5.1	2.1	2.8
26	5.5	2.3	3.0
28	5.9	2.5	3.3
31	6.5	2.8	3.7
33	6.9	3.0	3.9
35	7.2	3.1	4.1
38	7.9	3.4	4.5
40	8.2	3.6	4.7

EXAMPLE 23

10 A chelated spruce TMP was bleached with alkaline hydrogen peroxide in two stages to give a control BTMP pulp (abbreviated as P1P2). The first-stage (P1) bleaching was carried out using 2% H₂O₂, 1.5% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) at 60 °C and 10% consistency for 3 hours according to the general procedure C disclosed. The second-stage
15 (P2) bleaching was carried out using 4% H₂O₂, 3% NaOH, 3% Na₂SiO₃,

0.05% Mg (as MgSO_4) at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. The same chelated spruce TMP were also bleached in two stages with the same amount of bleaching chemicals, temperature, time and consistency except that either the P1 or P2-stage was carried out in the presence of 1.0% (OD pulp) of amino-HALS. Table 23 shows the PC numbers of the control P1P2, the P1P2 bleached pulps with P1 or P2 bleached in the presence of 1.0% (OD pulp) of amino-HALS versus the ambient light (light intensity = 85 ∇ 3 foot-candle) exposure times. Addition of amino-HALS to either P1 or P2-stage of a two-stage P1P2 bleaching of the spruce TMP pulps provides the bleached pulps with much improved brightness stability.

TABLE 23

PC Numbers of the Bleached TMP Pulps versus Light Exposure Times (days)			
Time (d)	P1P2 (control)	P1P2 with P1 bleached in the presence of amino-HALS	P1P2 with P2 bleached in the presence of amino- HALS
0	0.0	0.0	0.0
3	0.8	0.2	0.4
5	1.2	0.3	0.5
7	1.7	0.5	0.7
10	2.3	0.8	1.0
12	2.7	1.1	1.3
14	3.1	1.3	1.5
19	4.1	1.8	2.1
21	4.6	2.1	2.3
24	5.2	2.4	2.7
26	5.5	2.6	2.9
28	5.9	2.8	3.1
31	6.6	3.2	3.5
33	7.0	3.4	3.8
35	7.4	3.6	4.0
38	8.0	3.9	4.5
40	8.4	4.1	4.7

EXAMPLE 24

A chelated spruce TMP was bleached with alkaline hydrogen peroxide in two stages to give a control P1P2 pulp. The P1 bleaching was carried out using 2% H_2O_2 , 1.5% NaOH, 3% Na_2SiO_3 , 0.05% Mg (as MgSO_4) at 60 °C and 10% consistency for 3 hours according to the general procedure C disclosed. The P2 bleaching was carried out using 4% H_2O_2 , 3% NaOH, 3% Na_2SiO_3 , 0.05% Mg (as MgSO_4) at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. The same chelated spruce TMP was also bleached in two stages in the same manner except that after the P1 stage, the pulp was treated with 1.0% (OD pulp) of amino-HALS at room temperature and pH 6.5 – 7.0 for 3 hours according to the general procedure A disclosed. Table 24 shows the PC numbers of the control P1P2 pulp, and the P1P2 pulp that involved a treatment of the pulp with 1.0% (OD pulp) of amino-HALS after P1 and before P2 bleaching, versus the ambient light (light intensity = 85 ∇ 3 foot-candle) exposure times. Treatment of the P1 pulp with amino-HALS before the P2 stage provides the P1P2 pulp with much improved brightness stability.

TABLE 24

PC Numbers of the Bleached TMP Pulps versus Light Exposure Times (days)		
Time (d)	P1P2	P1/amino-HALS treatment/P2
0	0.0	0.0
2	0.6	0.2
5	1.3	0.5
7	1.7	0.7
9	2.1	0.9
14	3.2	1.5
16	3.6	1.7
19	4.4	2.2
21	4.7	2.4
23	5.1	2.6
26	5.8	3.0
28	6.2	3.3
30	6.7	3.6
33	7.2	4.0
35	7.7	4.2
37	8.1	4.5
40	8.7	4.9

EXAMPLE 25

A chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed to give a control BTMP. The same chelated spruce TMP pulps were also bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and, in the presence of 1.0% 4-amino-2,2,6,6-tetramethylpiperidine (abbreviated as amino-HALS), and 1.0% of % 4-oxo-2,2,6,6-tetramethylpiperidine (abbreviated as oxo-HALS), respectively, at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. Table 25 shows the PC numbers of the control BTMP, the BTMP pulps bleached in the presence of 1.0% (OD pulp) of amino-HALS and 1.0% (OD pulp) of oxo-HALS, respectively, versus the ambient light (light intensity = 85 ∇ 3 foot-candle) exposure times. Bleaching of the spruce TMP pulp in the presence of amino-HALS

but not oxo-HALS provides the bleached pulp with much improved brightness stability.

TABLE 25

PC Numbers of the BTMP Pulps versus Ambient Light Exposure Times (days)			
Time (d)	BTMP	BTMP bleached in the presence of amino-HALS	BTMP bleached in the presence of oxo-HALS
0	0.0	0.0	0.0
2	0.5	0.0	0.4
4	0.8	0.1	0.7
7	1.4	0.3	1.2
11	2.1	0.6	1.9
14	2.6	0.8	2.4
16	3.1	1.0	2.8
18	3.5	1.1	3.2
21	4.0	1.4	3.8
23	4.4	1.5	4.2
25	4.9	1.8	4.6
28	5.4	2.0	5.3
30	5.8	2.1	5.6
35	6.8	2.6	6.7
37	7.2	2.8	7.1
39	7.5	2.9	7.5
42	8.1	3.2	8.1

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EXAMPLE 26

A chelated spruce TMP was bleached with 5% H₂O₂, 4% NaOH, 3% Na₂SiO₃, 0.05% Mg (as MgSO₄) and, 0.0% (control) and 1.0% (OD pulp) of amino-HALS, respectively, at 60 °C and 20% consistency for 3 hours according to the general procedure C disclosed. A portion of a handsheet made from the control BTMP and a portion of a handsheet made from the BTMP bleached in the presence of amino-HALS were coated with 1.0% of 2,4-dihydroxybenzophenone (abbreviated as DHBP) (Aldrich) dissolved in ethanol. Table 26 shows the PC numbers of the control BTMP, the control BTMP coated with DHBP, the BTMP bleached in the presence of amino-HALS, and the BTMP bleached in the presence of amino-HALS and then

15

coated with DHBP versus the ambient light (light intensity = 85 ∇ 3 foot-candle) exposure times, respectively. A nearly complete brightness stabilization of the BTMP pulp can be achieved by bleaching of the pulp in the presence of amino-HALS and then by coating the sheet made from such a bleached pulp with an ultraviolet absorber such as DHBP.

TABLE 26

PC Number of the Bleached TMP Pulps versus Ambient Light Exposure Time (days)				
Time (d)	BTMP	BTMP coated with DHBP	BTMP bleached with amino-HALS	BTMP bleached with amino-HALS and coated with DHBP
0	0.0	0.0	0.0	0.0
2	0.5	0.1	0.0	-0.1
4	0.9	0.3	0.2	-0.1
7	1.4	0.6	0.4	0.0
9	1.8	0.7	0.5	0.0
11	2.2	0.9	0.7	0.1
14	2.8	1.2	0.9	0.2
18	3.6	1.7	1.3	0.4
21	4.1	2.0	1.5	0.5
23	4.5	2.2	1.8	0.6
25	4.9	2.3	1.9	0.6
28	5.5	2.7	2.2	0.7
30	5.8	2.8	2.3	0.8
32	6.2	3.0	2.5	0.8
35	6.8	3.4	2.8	0.9
37	7.1	3.5	3.0	1.0
42	8.1	4.0	3.5	1.2

EXAMPLE 27

10 Spruce BTMP pulps (ISO brightness 75.7%) were reacted with 1.0% (OD pulp) of 4-amino-TEMPO at room temperature and pH 6.5 - 7.0 according to the general procedure A disclosed, except without purging the pulp slurry with N₂ and that tap water (conductivity 25.2 μ S/cm) and a mill process water such as a mill peroxide bleaching filtrate containing

dissolving lignin (conductivity 3.47×10^3 :S/cm) were, respectively, used for the treatment and that tap water was used for the washing of the pulps. A same BTMP pulp was also reacted with 1.0% (OD pulp) of 4-amino-TEMPO in deionized water (conductivity 0.68 :S/cm) at room temperature and pH 6.5 – 7.0 according to the general procedure A disclosed, except without purging the pulp slurry with N₂. Table 27 lists the PC numbers of the original BTMP, the BTMP pulps reacted with 4-amino-TEMPO in the deionized (DI), tap and mill waters, respectively, versus ambient office light (light intensity = 85 ∇ 3 foot-candle) exposure times. Reaction of the pulps with 4-amino-TEMPO in tap or mill process water also provides the pulps with much improved brightness stability.

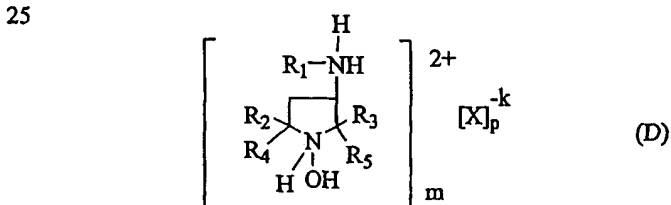
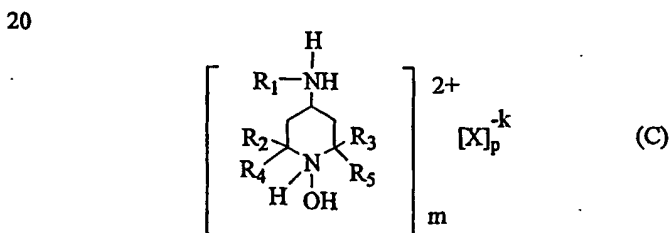
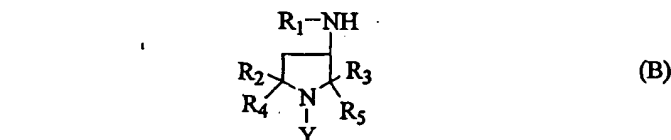
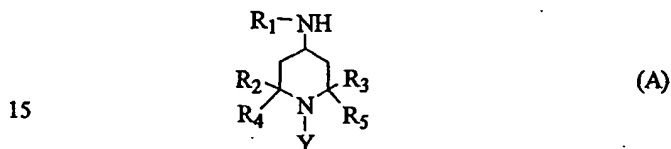
TABLE 27

PC number of the Bleached TMP Pulps versus Ambient Office Light Exposure Time (days)				
Time (d)	BTMP	BTMP reacted with inhibitor in DI water	BTMP reacted with inhibitor in tap water	BTMP reacted with inhibitor in mill water
0	0.0	0.0	0.0	0.0
2	0.7	-0.1	0.0	0.2
4	1.1	0.0	0.1	0.4
7	1.7	0.1	0.3	0.7
9	2.1	0.1	0.4	0.8
11	2.5	0.2	0.5	1.0
14	3.2	0.4	0.7	1.3
16	3.6	0.4	0.8	1.5
18	4.1	0.5	0.9	1.6
21	4.7	0.6	1.0	1.9
23	5.2	0.7	1.2	2.1
25	5.7	0.8	1.3	2.3
28	6.3	0.9	1.6	2.5
30	6.7	1.0	1.5	2.7
32	7.2	1.0	1.6	2.9
35	7.8	1.1	1.8	3.1
37	8.4	1.2	1.9	3.3

It is understood that the invention is not to be limited to the brightness stabilization of the various mechanical wood pulps described, as the invention can be applied to other lignin-containing mechanical wood pulps of the same or different wood species or to other lignocellulosic materials such as wood products by those skilled in the art.

CLAIMS

1. A method for the production of a light-stable, lignocellulosic material comprising reacting the material with a water-soluble, yellowing inhibitor possessing a primary or secondary amino group of the formula A, B, C or D wherein Y is oxyl (O[•]) or hydroxyl (OH) in an aqueous medium, or with a water-soluble hindered amine light stabilizer of the formula A or B wherein Y is hydrogen (H) in an alkaline peroxide bleaching medium or in an aqueous medium with a subsequent bleaching of the reacted material in an alkaline peroxide bleaching medium



wherein R_1 is hydrogen or an alkyl group $(CH_2)_nH$ that is unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl, and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber; R_2 , R_3 , R_4 and R_5 are independently alkyl groups $(CH_2)_nH$ that are unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl, and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber; X is an inorganic or organic anion, n is 1 to 14, preferably 1 to 6, and more preferably 1 to 4, k is 1 to 3, p is 1 or 2, M is an ammonium or metal ion and r is 1, 2 or 3, and the total charge of $2m$ is equal to kp .

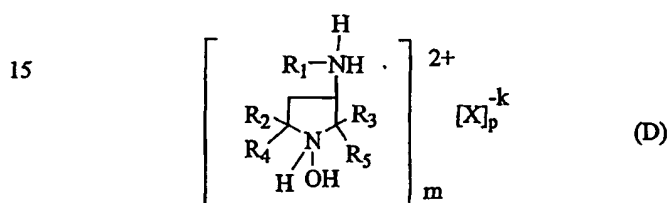
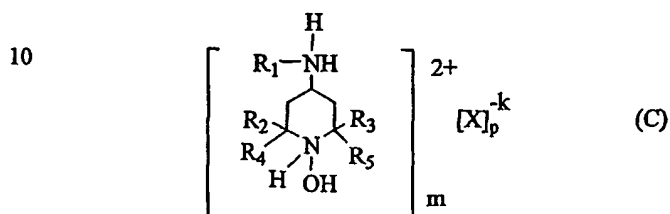
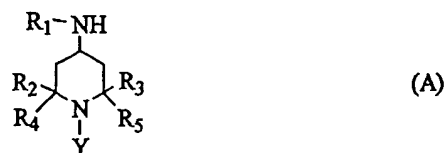
2. A method according to claim 1 wherein said material is reacted with said yellowing inhibitor in said aqueous medium.
3. A method according to claim 1 wherein said material is reacted with said stabilizer in said alkaline peroxide bleaching medium.
4. A method according to claim 1 wherein said material is reacted with said stabilizer in an aqueous medium with a subsequent bleaching of the reacted material in said alkaline peroxide bleaching medium.
5. A method according to any one of claims 1 to 4 wherein said lignocellulosic material is a wood pulp and including steps of forming a paper from the resulting pulp and coating the paper with an ultraviolet absorber.

6. A method according to claim 1, 2, 3 or 4 wherein at least one of R₁, R₂, R₃, R₄ and R₅ is a said alkyl group substituted with an organic ultraviolet absorber derived from 2,4-dihydroxybenzophenone or 2-hydroxybenzophenone.
- 5 7. A method according to any one of claims 1 to 6 wherein X is selected from carbonate, chloride, bisulfate, sulfate, formate, acetate, citrate, phosphate and ascorbate.
- 10 8. A method according to claim 1 or 2 wherein the yellowing inhibitor is 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl.
9. A method according to claim 1, 3 or 4 wherein the hindered amine light stabilizer is 4-amino-2,2,6,6-tetramethylpiperidine.
- 15 10. A method according to any one of claims 1 to 9 wherein the reaction of the lignocellulosic material is conducted with a charge of the yellowing inhibitor or hindered amine light stabilizer of 0.01 to 2.0%, by weight, based on the oven dry weight of the lignocellulosic material.
- 20 11. A method according to claim 10 wherein said amount is 0.2 to 1.0%, by weight.
- 25 12. A method according to any one of claims 1 to 11 wherein the reaction is conducted at a temperature of 20 – 120 °C, a consistency of 1.5 - 50%, and a time of 5 minutes to several days.
13. A method according to claim 1, 2 or 4 wherein the reaction in an

aqueous medium is conducted at a pH of 3.5 – 12.5.

14. A method according to claim 1 or 2 wherein a reducing agent or an acid is added to the reaction medium.
- 5
15. A method according to claim 1, 2, 3 or 4 wherein the material is a pulp and the resulting pulp is treated with a reducing agent or an acid.
- 10 16. A method according to any one of claims 1 to 13 wherein the reaction and/or bleaching is conducted in the presence or absence of air or oxygen.
- 15 17. A method according to claim 1, 3 or 4 wherein the lignocellulosic material is a mechanical wood pulp and the reaction is carried out in a single-stage or multi-stage in one or more than one refiner, bleach tower, pulp mixer, a storage vessel, or any other reaction vessel suitable for performing the alkaline hydrogen peroxide bleaching of the pulp.
- 20 18. A method according to any one of claims 1 to 9 wherein the lignocellulosic material is wood chips and at least one of said reacting and bleaching is carried out in a single-stage or multi-stage in one or more than one impregnator.
- 25 19. A method according to claim 18 wherein the impregnation of the wood chips is conducted at a temperature of 40 - 90 °C, a solid content of 30 - 60%, by weight, and an impregnation time of 5 minutes to 2 hours

20. A pulp produced by a method as defined in claim 1, 2, 3 or 4.
21. A pulp according to claim 20 wherein said lignocellulosic material is
5 a blended wood pulp.
22. A paper sheet containing a pulp of claim 20 or 21.
23. A paper sheet according to claim 22 containing said pulp as the sole
10 pulp component.
24. A paper sheet according to claim 22 containing said pulp in
conjunction with a chemical pulp.
- 15 25. A light stable lignocellulosic material comprising a lignocellulosic
material having a yellowing inhibitor of formula A, B, C or D
wherein Y is oxyl (O[·]) or hydroxyl (OH) covalently linked thereto
via a primary or secondary amino group of the inhibitor or stabilizer:



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wherein R_1 is hydrogen or an alkyl group $(CH_2)_nH$ that is unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl, and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber; R_2 , R_3 , R_4 and R_5 are independently alkyl groups $(CH_2)_nH$ that are unsubstituted or substituted by 1 to $2n+1$ number of a hydroxyl, ether, thio, thioether, benzyl, amino, ester, amide, carboxyl, and/or carboxylate $[(COO^-)_rM^{r+}]$ group, and/or radicals derived from an organic ultraviolet absorber; X is an inorganic or organic anion, n is 1 to 14, preferably 1 to 6, and more

preferably 1 to 4, k is 1 to 3, p is 1 or 2, M is an ammonium or metal ion and r is 1, 2 or 3, and the total charge of 2m is equal to kp.

26. A material according to claim 25 wherein the lignocellulosic material is a mechanical wood pulp.

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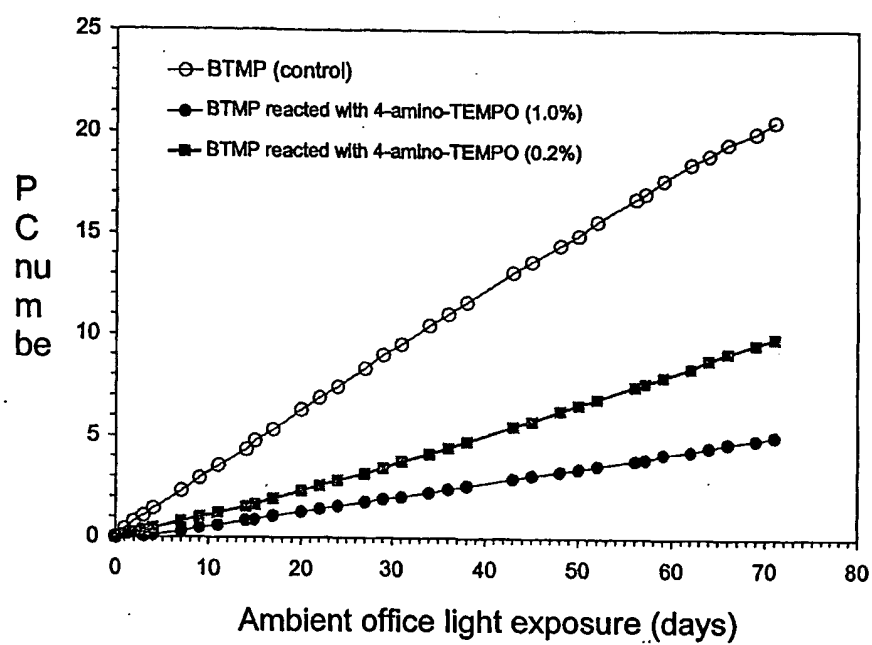


Fig. 1

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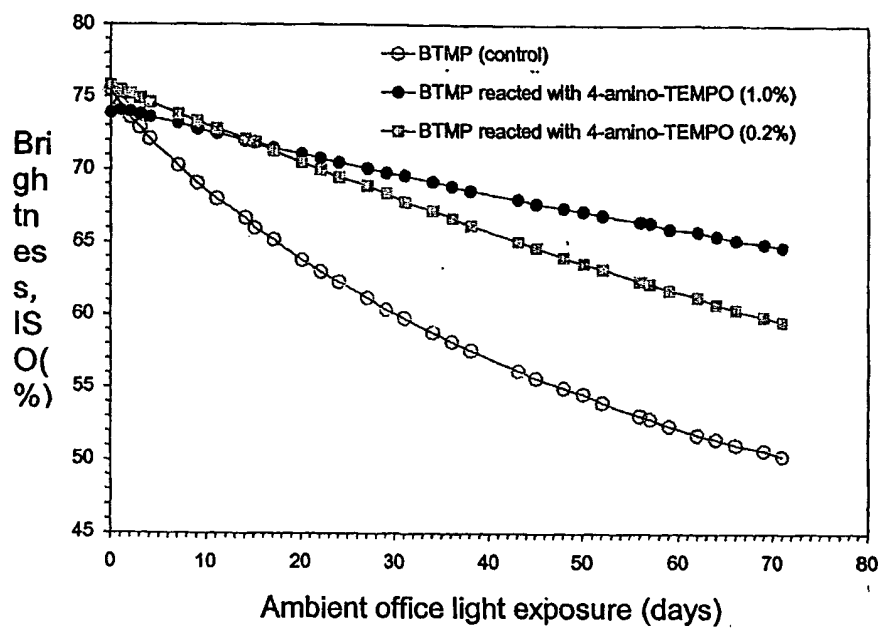


Fig. 2

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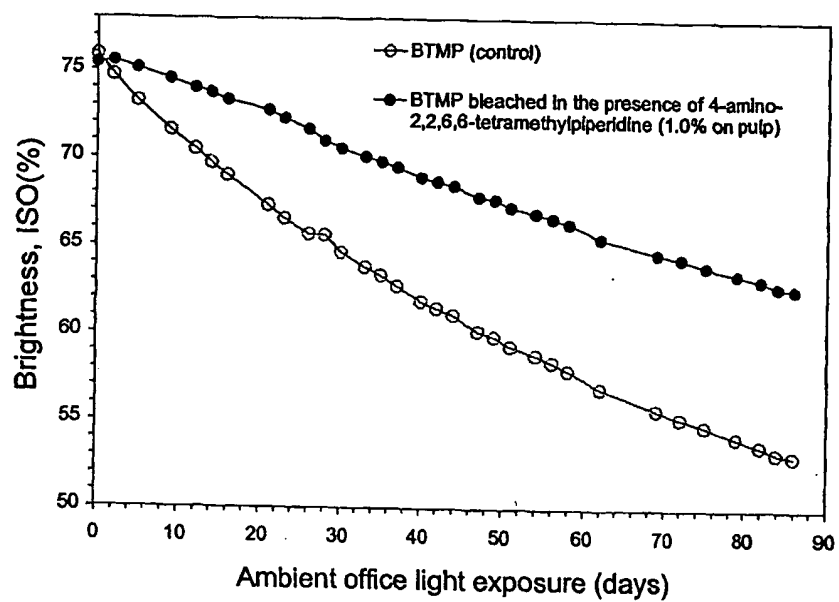


Fig. 3

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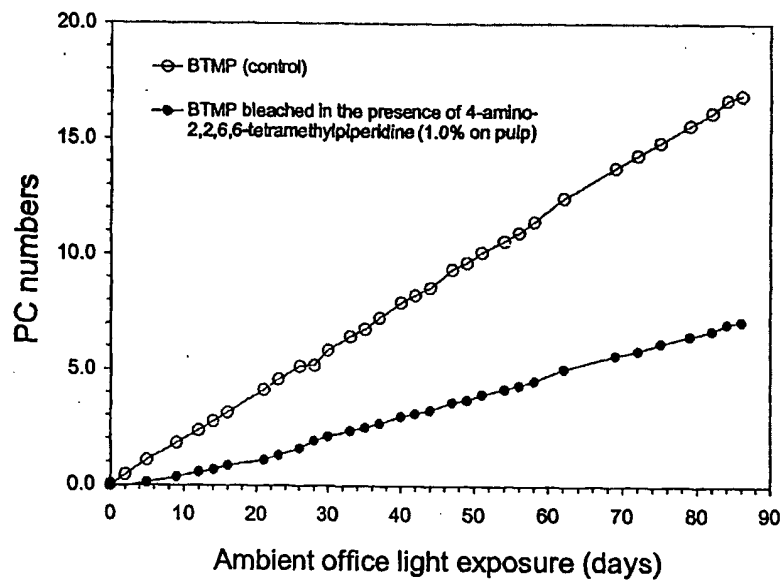


Fig. 4